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THE THEORY OF THE CHRISTIANSEN EXPERIMENT

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1. Introduction

In the well-known experiment due to Christiansen (1884), an optically isotropic solid, *e.g.*, glass, is powdered and put inside a flat-sided cell which is then filled with liquid and the refractive index of the latter is adjusted suitably by varying its composition or altering its temperature. Beautiful chromatic effects are observed when the refractive index of the liquid is thus brought into coincidence with that of the powder for some chosen wave-length in the spectrum. The cell becomes transparent for a restricted region of the spectrum in the vicinity of that wave-length, while the rest of the incident light passing through the cell is diffused out in various directions and appears as a halo surrounding the light source. The range of wave-lengths regularly transmitted by the cell diminishes as its thickness is increased and is also influenced by the other conditions of the experiment. Coarser powders give a sharper transmission band, while, *per contra*, the range of wave-lengths transmitted may be made as large as we please by making the particles sufficiently fine. The difference in the dispersive powers of the solid and the liquid is also of importance. When it is large, the transmission band is sharp, while *per contra*, if it be small enough, nearly the whole spectrum can get through.

From the facts stated, it is clear that the effects observed in the Christiansen experiment are not capable of being understood on a purely geometric basis but require to be considered on the basis of wave-optics. This was appreciated by Rayleigh (1899), and he suggested that by considering the fluctuations in the number of particles encountered by a ray of light traversing the cell and the resulting variations in optical path, it might be possible to make a theoretical estimate of the width of the transmission band in the spectrum. The subject was, however, not further pursued by him. At the suggestion of the present writer, N. K. Sethi (1920) undertook a study with a view to obtain some experimental data and develop a theory capable of explaining the facts. A considerable measure of success was achieved by him in both of these directions. His work was followed up by C. M. Sogani (1926), who made a detailed examination of the optical phenomena exhibited by the so-called chromatic emulsions. Later,

B. Mukhopadhyaya (1932) undertook to investigate the case of very finely powdered non-isotropic crystals. More recently, also, G. N. Ramachandran (1943) has sought to elucidate the subject further by considering the case in which the particles are of spherical shape and applying to it the principles of diffraction theory.

The present paper considers the subject afresh from a point of view which is different from that originally suggested by Rayleigh and is also simpler. The theory as now developed gives us a clear account of the phenomena and yields results in satisfactory accord with the facts of observation. Its publication has appeared desirable in view of the fact that of recent years, the importance of the Christiansen effect has been more widely appreciated. Many papers have been published and many references to it have appeared in text-books, concerning themselves chiefly with its practical application in optical filters capable of isolating narrow regions in the spectrum with the minimum loss of light. Strangely enough, however, one does not find in the literature of the subject any recognition of the fact that the performance of such a filter is determined by the principles of wave-optics.

2. Some General Considerations

The powder-liquid mixture contained in a Christiansen cell is an optically heterogeneous medium, and its functioning depends on the fact that while this heterogeneity vanishes for the particular wave-length for which the two refractive indices (μ_1 of powder and μ_2 of liquid) are identical, it persists for adjoining wave-lengths and disturbs the regular wave-propagation in their cases. In actual practice, the thickness of a Christiansen filter is of the order of a centimetre or even several centimetres, and hence, we shall not be justified in assuming a simple rectilinear propagation of the light rays for such wave-lengths through the entire distance. To find the effect of the cell on the passage of the incident light-beam, we have to conceive of its total thickness as divided up into a sufficiently large number of individual layers, each of which in its turn produces its own independent effect, namely that of diverting part of the energy of the incident wave-train away from its original path in the form of diffracted waves. The wave-train finally emerging from the cell is that which has had its intensity cut down in this manner by the cumulative effect of the successive layers through which it has passed. To complete the picture, one has also to consider the diffracted radiations having their origin at these layers and emerging from the cell, since they are responsible for the halo observed in the experiment. The characters of the halo would evidently be determined by the intensities of these radiations as well as by their distribution in angle for various wave-lengths.

In considering the problem from the point of view indicated above, it is evident that various quantities need to be known, *viz.*, the size, shape and orientation of the particles of the powder, as well as the manner in which they are disposed within the cell with respect to their neighbours. In the circumstances of the actual experiment, however, none of these quantities can be considered as invariable. It is precisely this situation which justifies us in adopting the approach indicated above and dividing up the thickness of the cell into a large number of layers which could be considered as acting more or less independently of each other. Layers of the same thickness would not necessarily be similar in their behaviour, but such differences would be averaged out when the total effect of the whole cell is under consideration. Hence, it is permissible to base our discussion on the behaviour of a single layer which is representative of the material contained in the cell. The question arises as to what should be the choice for the thickness Δ of an elementary layer, if the theory developed on these assumptions should correctly describe the facts. It is obvious that the fluctuations in optical path arising within a given layer would be *relatively* the largest when its thickness is smallest. On the other hand, it would be clearly not permissible to carry the subdivision beyond the point at which the dimensions of an individual particle would exceed Δ. The choice which we shall accordingly make for Δ is that it is equal to the maximum distance which a light ray could travel within a single particle of average dimensions contained in the cell.

3. Formulation of the Theory

By way of introducing the most general case, we shall first consider a particular example in which the elementary layers are assumed to be so constituted as to produce the maximum disturbance of the wave-propagation. This would obviously be the case when the entire thickness Δ of an elementary layer is occupied at various points on its area either by the solid alone or by the liquid alone, one-half of the aggregate area being thus occupied by the solid material and the other half by the liquid. The retardation of the wave-front in its passage through the layer would be $\mu_1\Delta$ in one case and $\mu_2\Delta$ in the other. Hence, if the wave-train before entry normally into the layer is represented by

$$\sin \frac{2\pi}{\lambda}(ct - Z) \tag{1}$$

the wave-train emerging from it is given by the summation

$$\tfrac{1}{2} \sin \frac{2\pi}{\lambda}(ct - Z - \mu_1\Delta) + \tfrac{1}{2} \sin \frac{2\pi}{\lambda}(ct - Z - \mu_1\Delta)$$

and may therefore be written as

$$\cos \frac{\pi(\mu_1 - \mu_2)\Delta}{\lambda} \sin \frac{2\pi}{\lambda}(ct - Z - \tfrac{1}{2}\Delta \cdot \overline{\mu_1 + \mu_2}) \tag{2}$$

The loss of intensity of the wave-train in its passage through the layer is obtained by squaring the amplitudes in (1) and (2) and taking the difference. It is evidently

$$\sin^2 \frac{\pi(\mu_1 - \mu_2)\Delta}{\lambda} \tag{3}$$

while the retardation in phase produced by the layer is

$$\frac{\pi(\mu_1 + \mu_2)\Delta}{\lambda}. \tag{4}$$

The retardation in phase produced by passage through the entire cell would be merely the sum of the retardations produced by the individual layers. On the other hand, the reduction in intensity would be cumulative. It may be found by writing (3) in the form of a differential equation for the reduction of intensity, *viz.*,

$$dI = -I \cdot \sin^2 \pi(\mu_1 - \mu_2)\Delta/\lambda \cdot dz/\Delta \tag{5}$$

On integrating (5) we obtain

$$I = I_0 \cdot e^{-\sin^2 \pi(\mu_1 - \mu_2)\Delta/\lambda \cdot z/\Delta}, \tag{6}$$

where z is the total thickness of the cell and Δ may be identified with the effective thickness of the particles of the powder. As an approximation, we may write (6) in the form

$$I = I_0 \cdot e^{-\pi^2(\mu_1 - \mu_2)^2 \Delta z/\lambda^2} \tag{7}$$

We may now readily generalize the foregoing treatment. For this purpose, we divide the cell-thickness as before into elementary layers of thickness Δ. Considering an individual layer of this thickness, we imagine its area divided into a large number N of equal parts. The disturbance incident normally on the layer being

$$\sin \frac{2\pi}{\lambda}(ct - Z)$$

the regularly emergent wave-train is given by the summation of the disturbances emerging from all the N elements of area, *viz.*,

$$\sum_N \sin \frac{2\pi}{\lambda}(ct - Z - \mu\Delta), \tag{8}$$

where μ is a quantity defined for each of the N elementary areas of the wave-front by the relations

$$\mu\Delta = \mu_1\Delta_1 + \mu_2\Delta_2 \text{ and } \Delta_1 + \Delta_2 = \Delta. \tag{9}$$

Δ_1 and Δ_2 are the paths traversed in solid and liquid respectively in the particular area. On effecting the summation indicated in (8) and evaluating the resulting intensity, we find the diminution produced by passage through the layer to be

$$\frac{4}{N^2} \cdot \sum_{rs} \sin^2 \frac{\pi (\mu_r - \mu_s) \Delta}{\lambda}, \tag{10}$$

where μ_r and μ_s are the values of μ respectively at two different elements of area and the summation indicated in (10) is made over all such pairs of elements, $N^2/2$ in number. We may, at this stage, make an approximation and write (10) in the form

$$\frac{4}{N^2} \sum_{rs} \cdot \frac{\pi^2 (\mu_r - \mu_s)^2 \cdot \Delta^2}{\lambda^2} \tag{11}$$

If k_{rs} is a number defined by the relation

$$k_{rs} (\mu_1 - \mu_2) = (\mu_r - \mu_s) \tag{12}$$

and using the abbreviation

$$k^2 = \frac{4}{N^2} \sum_{rs} k_{rs}^2 \tag{13}$$

we may write (11) in the form

$$k^2 \pi^2 (\mu_1 - \mu_2)^2 \cdot \Delta^2/\lambda^2. \tag{14}$$

Finally, by integration over the whole thickness of the cell, we obtain as the expression for the transmission coefficient

$$e^{-k^2 \pi^2 (\mu_1 - \mu_2)^2 \cdot \Delta z/\lambda^2} \tag{15}$$

Our final formula (15) thus differs from (7) obtained earlier for an idealized case merely by the appearance of an additional numerical factor k^2 in the exponential. That this factor has a maximum value of unity and would in general be rather less may be shown by considering particular examples. If, for instance, $\mu\Delta$ is $\mu_1\Delta$ over σN elements of area of the wave-front and $\mu_2\Delta$ for the remaining $(1 - \sigma)$ N elements, we obtain at once from (12) and (13) that

$$k^2 = 4\sigma (1 - \sigma). \tag{16}$$

k^2 has thus the maximum value unity when $\sigma = \frac{1}{2}$, as in the case considered earlier. That k^2 would be less than unity when the thickness of the individual particles is less than Δ over a part of their area, is also fairly obvious on a consideration of the effect on the summations indicated in (12) and (13).

4. The Case of Spherical Particles

It is of interest to consider the special case in which the particles of the powder are tiny spheres, since it forms an excellent illustration of the general theory, and also since it is an experimentally realisable case. We consider

a layer of thickness Δ equal to the diameter of the spherules in which a fraction σ of the area of the wave-front is covered by the spherules, while in the remaining fraction $(1-\sigma)$ the light passes entirely through the surrounding liquid. The disturbance emerging from the layer may be written in the form

$$(1-\sigma)\sin\eta + \sigma\int_0^{\pi/2} 2\sin(\eta - \xi\cos\theta)\sin\theta\cos\theta d\theta \tag{17}$$

where

$$\eta = \frac{2\pi}{\lambda}(ct - Z) \text{ and } \xi = \frac{2\pi(\mu_1 - \mu_2)\Delta}{\lambda} \tag{18}$$

The integration may be effected, enabling (17) to be written as

$$(1-\sigma)\sin\eta + 2\sigma\sin\eta\left[\frac{\sin\xi}{\xi} + \frac{\cos\xi}{\xi^2} - \frac{1}{\xi^2}\right] + 2\sigma\cos\eta\left[\frac{\cos\xi}{\xi} - \frac{\sin\xi}{\xi^2}\right] \tag{19}$$

It is readily verified that in the limit when ξ is zero, (19) reduces to $\sin\eta$, as it should. We are interested in the cases when ξ is rather small, and (19) may then be written in the approximate form

$$(1 - \sigma \,.\, \xi^2/4)\sin\eta - \sigma \,.\, 2\xi/3 \,.\, \cos\eta \tag{20}$$

Finally, we obtain for the coefficient of transmission, an expression of the same form as the general formula (14) in which the constant k^2 is given by

$$k^2 = (2\sigma - 16\sigma^2/9). \tag{21}$$

This has a maximum value 9/16 when $\sigma = 9/16$; in other words when the spherules cover a little over half the area in each layer. It is thus apparent that the spherical shape of the particles would result in a very considerable increase in the spectral width of the transmission band as compared with the case in which the particles are flat platelets.

5. The Diffraction Halo

That the halo seen surrounding the source of light in the Christiansen experiment is a diffraction effect, and not a simple matter of geometrical optics should be evident from the fact that it has its origin in the same set of circumstances which determine the spectral range of the regularly transmitted light, *viz.*, the optical heterogeneity of the medium and its variations with wave-length. As remarked earlier in the paper, the halo is, in essence, a superposition of the diffracted radiations having their origin in the successive layers within the cell traversed by the incident beam of light.

In considering the problem of the distribution of light in the halo and the spectral character of the radiations composing it, it should be emphased that the diffracted radiations have their origin at the *layers* parallel to

the wave-front traversed by it, and hence that they represent the joint effect of all the particles in a layer. In other words, we have to consider the configuration of the whole wave-front after it has traversed the layer; the positions of the individual particles in the layer would determine the locations of the elevations or depressions (as the case may be) on the wave-front, while the size and shape of the particles and the value of $(\mu_1 - \mu_2)$ for the particular wave-length would determine their magnitude. In effect, each layer would form a two-dimensional laminar diffraction grating, though necessarily an irregular one. The theory of the haloes observed in the Christiansen experiment would thus be based on a description of the optical behaviour of such an irregular grating.

The theory of diffraction gratings has been well studied in the cases in which the rulings are regular and run in one direction only. We are here concerned with phase-change gratings, and the optical behaviour of such gratings may be readily described in terms of a quantity ζ which corresponds to $\pi (\mu_1 - \mu_2) \Delta/\lambda$ in our problem and represents the amplitude of the (harmonic) corrugations on the wave-front expressed as a phase-angle. When ζ is zero, the wave-front is plane and all the spectra vanish. When ζ is finite but small, only the first-order spectra on either side appear. Their intensity increases steadily as ζ increases and is quite considerable when ζ reaches the value 1, while the intensity of the higher order spectra is still quite small. The intensity of the first order spectra continues to increase till ζ is nearly equal to 2. At this stage, the second order has gained considerable strength, though still weaker than the first order, and the two orders between them contain nearly the whole of the incident energy. As ζ increases further, the spectra of still higher orders successively gain in strength, the orders having the maximum intensity being higher, the larger ζ is. The energy is distributed between several high orders for large values of ζ, so that individually they are rather weak.

The nature of the results to be expected in our present problem would necessarily be somewhat modified by various considerations. Nevertheless, one can indicate in general terms what they would be, on the basis of the results indicated above for a regular phase-change diffraction grating. Firstly, the diffracted radiations would be absent for the wave-length of maximum transmission for which $(\mu_1 - \mu_2)$ vanishes. They would rapidly increase in intensity as $(\mu_1 - \mu_2)$ becomes numerically larger and attain large values, but provided $(\mu_1 - \mu_2)$ is not too large, they would be concentrated principally in directions adjacent to that of regular transmission, the angular separation from it being determined by the average distance apart of the individual particles. (In a close-packed arrangement, this would also

be the size of the individual particles.) As $(\mu_1 - \mu_2)$ increases numerically beyond a certain limit, the diffracted radiations would spread out over a wider range of angles, and the direction of their maximum intensity would also move away further from that of regular transmission. Their intensity in any particular direction would simultaneously be much weakened.

Superficially, the results inferred above on the basis of diffraction theory resemble those which one might anticipate on the basis of geometrical optics as the result of irregular refractions by the particles of powder immersed in the surrounding liquid. Actually, however, they are different, since according to geometrical optics, the deviations of the rays would be determined by the *shape of the particles*, while in diffraction theory, it is *the size of the particles and their distances apart* in relation to the wave-length of light that principally determine the results.

6. Comparison with the Facts

That the transmission band of a Christiansen cell does not exhibit a sharp cut-off in the spectrum in either direction was observed by Sethi (*loc. cit.*) in his investigations on the subject. He noticed that the visually observed spectral width could be increased by merely increasing the intensity of the light incident on the cell, and inferred from this that the transmission curve resembled a graph of the Gaussian error function. This was verified quantitatively by decreasing the intensity of the incident light by known large fractions and observing the corresponding decrease in width of the transmission band. Using powdered glass in which the particles had been sorted out into grades of different size, and also using varying thicknesses of the cell, he was enabled to establish that the variable which determined the spread of the exponential curve was proportional to the product of the thickness of the cell and the size of the particles. Finally, combining these observations with theoretical considerations of the kind indicated by Rayleigh (*loc. cit.*), Sethi derived a formula identical with our formula (7) above, except that an empirical constant appeared in the exponential instead of π^2. Sethi remarks that his data indicated the constant to be about 7. Sogani (*loc. cit.*) carried the matter further and sought to evaluate the constant appearing in the formula theoretically. Considering the case in which the particles had a spherical shape and occupied the largest possible fraction of the total volume, he calculated the constant to be $16\pi^2/9$ or 18, while his experimental observations showed the constant to be about 9. According to Ramachandran (*loc. cit.*), the theoretical value of the constant is 22 for the same case, obviously much in excess of that indicated by the actual facts. It is noteworthy that the formula of Mukhopadhyaya (*loc. cit.*) when evaluated

gives the constant as about 5. The lower value is to be traced to his theoretical approach being more like that adopted in the present paper.

The general form of the transmission curve indicated by our theoretical formula (15) is thus supported by the experimental facts. Various authors have remarked upon the unsymmetrical form of the transmission curve which is steeper on the side of shorter wave-lengths than on the long wave-length side. This effect, according to our formula, would be due to the joint effect of two factors, *viz.*, due to $(\mu_1 - \mu_2)^2$ appearing in the numerator of the exponential increasing more rapidly towards shorter wave-lengths and also due to the factor λ^2 appearing in the denominator. The increased sharpness of the transmission band when it is pushed towards shorter wave-lengths by altering the temperature or varying the composition of the liquid, which has also been noticed in experiment, may similarly be explained as the joint effect of the same two factors in our theoretical formula. The appearance of λ^2 in the denominator is characteristic of wave-optics, and it is much to be desired that the influence of this factor is demonstrated by fresh quantitative data obtained with suitable material with which the transmission band could be shifted over a wide range of wave-lengths, and by disentangling therefrom the effect of the variations of the factor $(\mu_1 - \mu_2)^2$ which appear simultaneously. In respect of the other factors, *viz.*, the thickness of the cell and the size of the particles, the data already on record amply establish their influence. It would be desirable however to carry out further studies enabling the constant appearing in the formula to be evaluated in a number of cases, with a view to demonstrate the influence of the particle shape and of the closeness of packing on its numerical value.

In the practical use of a Christiansen filter, it is necessary, among other things, by suitable methods to separate the light regularly transmitted by the filter from that diffused or scattered by it. The discussion in the preceding section of the characters of the diffraction halo has an important bearing on this question. If the particles are very large, the diffracted light would appear in directions very close to that of the regularly transmitted light, and its separation from the latter would obviously become difficult. If, on the other hand, the particles are very small, the spectral width of the transmission would itself be greatly increased. There is thus an optimum size for the particles if the filter is to function most usefully. The work of Denmark and Cady (1935) is of interest in this connection. It may be remarked that the characters of the halo in directions adjacent to that of the transmitted light, as also in directions remote therefrom were very fully described and illustrated by a series of spectrograms in Sethi's paper of 1920. The features described by him find a satisfactory explanation on our present theory.

SUMMARY

The effects exhibited by a Christiansen filter can only be explained or understood in terms of wave-optics. A theoretical formula is derived in the paper for the distribution of intensity in the spectrum of the transmitted light, the variables involved being the wave-length of the light, the average size of the particles of the powder, the thickness of the cell and the difference in the refractive indices of the powder and the liquid for the wave-length under consideration. The characters of the halo observed around the light source are also discussed in terms of diffraction theory. The theory explains the facts of observation in a very simple manner and gives results in satisfactory accord with the available experimental data.

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ON AN INEQUALITY CONCERNING ORTHOGONAL POLYNOMIALS

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1. *Introduction.*—In a recent note,[1] G. Szegö has given several proofs of the following inequality of P. Turán for Legendre polynomials:—

$$\Delta_n(x) = P_n^2 - P_{n-1} P_{n+1} \geqslant 0 \tag{1}$$

and has pointed out that the inequality holds also for the Hermitian, the Laguerre and the ultraspherical polynomials. We show in this note that an elementary proof of the inequality may be given merely by considering the second derivative of $\Delta_n(x)$. This is done below for the Legendre, Hermitian and Laguerre polynomials. We follow the notation of G. Szegö: *Orthogonal Polynomials*, 1939.

2. *Legendre Polynomials.*—By differentiating $\Delta_n(x)$ and using the relations

$$(n+1) P_{n+1} - (2n+1) x P_n + n P_{n-1} = 0 \tag{2}$$

$$(1-x^2) P_n'(x) = n (P_{n-1} - x P_n) \tag{3}$$

we find, after some reduction,

$$\Delta''_n(x) = -\frac{2}{n(n+1)} \{P_n'(x)\}^2 \tag{4}$$

Thus $\Delta_n''(x) \leqslant 0$, and so $\Delta_n'(x)$ is a decreasing function of x. Now $\Delta_n(+1) = \Delta_n(-1) = 0$ and so, by Rolle's theorem, $\Delta_n'(x)$ must have at least one root in $(-1, +1)$; but, since $\Delta_n'(x)$ is a decreasing function in $(-1, +1)$, it can not have more than one root in that interval. Let $x = \xi$ be this root, so that $\Delta_n'(\xi) = 0$, $(-1 < \xi < +1)$. Then it is clear that $\Delta_n'(x) \geqslant 0$ in $-1 \leqslant x \leqslant \xi$ and $\Delta_n'(x) \leqslant 0$ in $\xi \leqslant x \leqslant 1$. Hence $\Delta_n(x)$ is an increasing function in $(-1, \xi)$ and a decreasing one in $(\xi, +1)$. Since $\Delta_n(-1) = \Delta_n(+1) = 0$, it follows that $\Delta_n(x) \geqslant 0$ in $(-1, +1)$, which establishes (1).

3. *Hermitian Polynomials.*—Since the interval of orthogonality for the Hermitian polynomials is $(-\infty, +\infty)$, it is convenient to introduce a new

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[1] G. Szegö, *Bull. Amer. Math. Soc.*, 1948, **54**, No. 4.

function $h_n(x)$ defined by

$$h_n(x) = e^{-x^2/2} H_n(x) \tag{5}$$

so that

$$h_n(x) \to 0 \text{ as } x \to \pm \infty \tag{6}$$

The relations

$$H_{n+1} - 2xH_n + 2nH_{n-1} = 0 \tag{7}$$

$$H_n'(x) = 2nH_{n-1} \tag{8}$$

expressed in terms of the h_n become

$$h_{n+1} - 2xh_n + 2nh_{n-1} = 0 \tag{9}$$

$$h_n'(x) = 2nh_{n-1} - xh_n \tag{10}$$

If we now set

$$f(x) = h_n^2 - h_{n-1} h_{n+1} = e^{-x^2} (H_n^2 - H_{n-1} H_{n+1}) = e^{-x^2} \Delta_n(x) \tag{11}$$

we find, by differentiating (11) and using (9) and (10),

$$f'(x) = -2h_{n-1} h_n \tag{12}$$

$$f''(x) = 2(h_n^2 - 2nh_{n-1}^2) \tag{13}$$

The relative maxima and minima of $f(x)$ are given by $f'(x) = 0$, *i.e.*, by the roots of $h_{n-1}(x) = 0$ and $h_n(x) = 0$. From (13) we see immediately that $h_n(x) = 0$ gives maxima, while $h_{n-1}(x) = 0$ gives minima. We further see that $f > 0$ at all the maxima and minima. This is obvious for the minima ($h_{n-1} = 0$); for the maxima ($h_n = 0$), $f > 0$ because then h_{n-1} and h_{n+1} are of opposite signs. Thus $f(x)$ has all its relative minima (and maxima) positive. In view of the fact that $f(x)$ and its derivatives are continuous, it is easy to conclude from this that f has a positive lower bound. Hence, $f(x) \geqslant 0$ for all x, which implies $\Delta_n(x) \geqslant 0$.

4. *Laguerre Polynomials.*—Here we set

$$l_n(x) = e^{-x/2} L_n(x), \; L_n(x) = \frac{e^x}{n!} \frac{d^n}{dx^n} (e^{-x} x^n) \tag{14}$$

The relations

$$(n+1) L_{n+1} - (2n + 1 - x) L_n + nL_{n-1} = 0 \tag{15}$$

$$xL_n'(x) = n(L_n - L_{n-1}) \tag{16}$$

then give

$$(n+1) l_{n+1} - (2n + 1 - x) l_n + nl_{n-1} = 0 \tag{17}$$

$$xl_n'(x) = \left(n - \frac{x}{2}\right) l_n - nl_{n-1} \tag{18}$$

If, as before, we write

$$f(x) = l_n^2 - l_{n-1} l_{n+1} = e^{-x} (L_n^2 - L_{n-1} L_{n+1}) = e^{-x} \Delta_n(x) \tag{19}$$

we find now the following results:—

$$f(0) = 0,\ f(x) \to 0 \text{ as } x \to +\infty \tag{20}$$

$$xf'(x) = (l_{n+1} - l_n)(l_n - l_{n-1}) \tag{21}$$

Thus the relative minima and maxima of $f(x)$ in $(0, \infty)$ are given by the positive roots of

$$l_{n+1} = l_n \text{ and } l_n = l_{n-1} \tag{22}$$

For $l_{n+1} = l_n$, we have $f = l_n^2 - l_{n-1} l_n = l_n (l_n - l_{n-1})$

$$= \frac{x}{n} l_n^2, \text{ by (17)}$$

and similarly, for $l_n = l_{n-1}$, $\quad f = \frac{x}{n+1} l_n^2$ $\Bigg\}$ (23)

so that all relative minima and maxima of $f(x)$ are positive for $x > 0$.

Actually we may easily verify by further differentiation that

$$f''(x) = \frac{1}{n+1} l_n^2 \text{ for } l_n = l_{n-1}$$

$$= -\frac{1}{n} l_n^2 \text{ for } l_{n+1} = l_n \Bigg\} \tag{24}$$

so that $l_n = l_{n-1}$ gives minima and $l_{n+1} = l_n$ gives maxima of $f(x)$. It then follows as in the case of the Hermitian polynomials that

$$\Delta_n(x) = L_n^2 - L_{n-1} L_{n+1} \geqslant 0,\ x \geqslant 0.$$

5. The same method can be applied to show that the inequality in question holds also for the ultraspherical polynomials $P_n^{(\lambda)}(x)$ and the generalised Laguerre polynomials $L_n^{(\alpha)}(x)$ under suitable restrictions on the values of λ and α.

A METHOD OF DISTINGUISHING BETWEEN FLAVONES AND FLAVONOLS

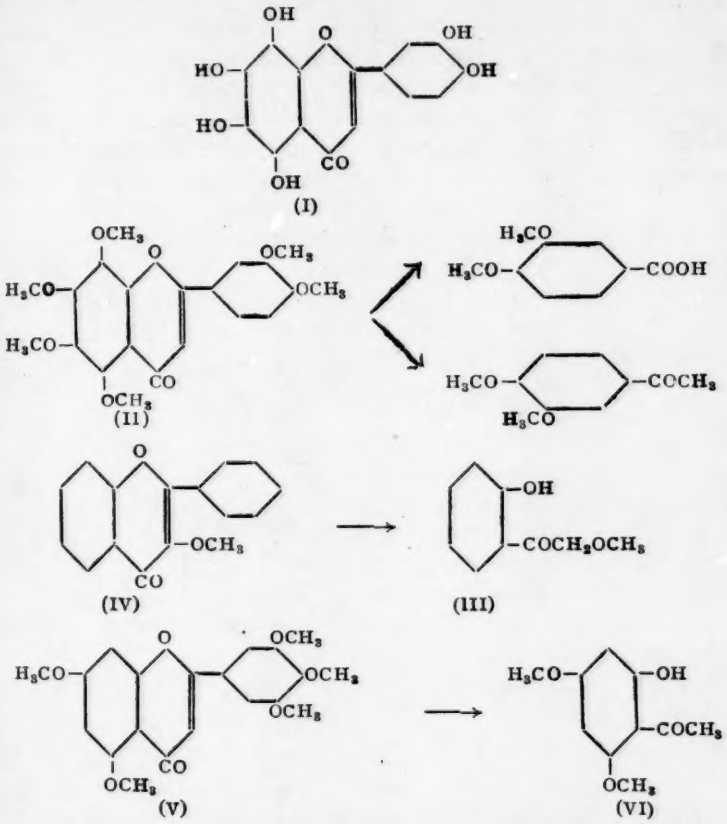
By K. J. Balakrishna, N. Prabhakara Rao and T. R. Seshadri

(From the Department of Chemistry, Andhra University, Waltair)

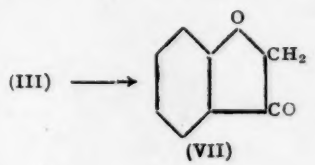
Received March 28, 1948

In the investigation of the naturally occurring anthoxanthins, a satisfactory method of distinguishing between flavones and flavonols was found necessary. Colour reactions, dyeing properties, absorption spectra and stability to aerial oxidation in alkaline solution have been used in the past fairly successfully, but their use becomes limited when the entire range of variation in types is taken into consideration. For example, stability to aerial oxidation could be mentioned. According to Perkin,[1] whereas as a rule hydroxy-flavones are not oxidised by air in alkaline solution and precipitated therefrom unchanged by acids, flavonols on the other hand are readily decomposed in this manner with the formation of water-soluble products. But when the molecule contains a large number of hydroxyl groups as in nor-nobiletin (flavone I), instability to this treatment arises even in flavones. A more satisfactory procedure is to effect complete methylation and subject the fully methylated ether to fission with aqueous or alcoholic alkali. The side-phenyl nucleus is obtained in both cases as a substituted benzoic acid satisfactorily. Under suitable conditions it has been possible to obtain this part of the molecule in the case of flavones as a substituted acetophenone also, in a small yield. In this manner Robinson and Tseng[2] could identify veratric acid and aceto-veratrone among the products of decomposition of nobiletin (II) with aqueous alcoholic potash and the formation of the ketone was considered to be a definite proof that nobiletin was a flavone. On the other hand, to obtain the condensed benzene ring as a substituted acetophenone (III) is more often a characteristic of flavonols (IV). Such a behaviour can however be found with flavones also. For example, tricin-trimethyl ether (V) yields phloracetophenone dimethyl ether (VI) by this method of hydrolysis.[3]

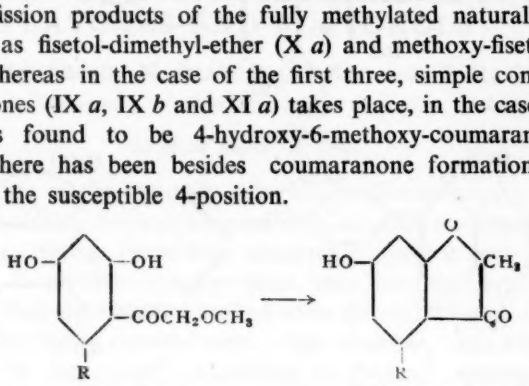
Though there is difficulty in making a distinction between flavones and flavonols simply from the manner of their fission with alkali it could be seen that the presence of an ω-methoxyl group in the ketonic fission product (III) representing the condensed benzene ring is definitely a characteristic of flavonols. The detection of this structural feature offers, therefore, an unfailing method of distinction.



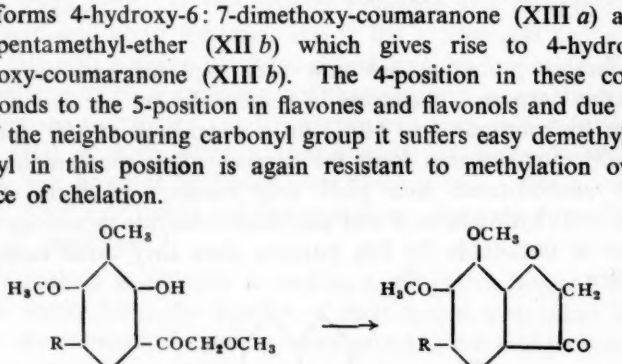
A satisfactory procedure has now been explored and shown to be suitable for this purpose. It consists in heating the ketonic fission product with aqueous hydrobromic acid (40%) on a water-bath at 100° for about 3 hours. ω-Methoxy-ketones form the corresponding coumaranones (VII) whereas the unsubstituted ones yield only resinous products. Stronger hydrobromic acid, hydriodic acid and aluminium chloride in various solvents are found to be unsuitable for this purpose since they cause considerable resin-formation.



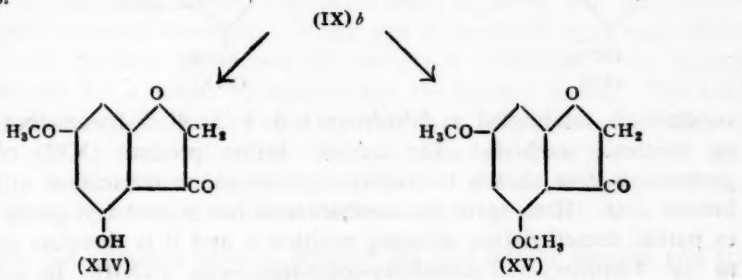
This reaction has been first examined using simpler cases like ω-methoxy-resacetophenone (VIII *a*) and ω-methoxy-phloracetophenone (VIII *b*) and also with the fission products of the fully methylated naturally occurring flavonols such as fisetol-dimethyl-ether (X *a*) and methoxy-fisetol-dimethyl-ether (X*b*). Whereas in the case of the first three, simple conversion into the coumaranones (IX *a*, IX *b* and XI *a*) takes place, in the case of the last, the product is found to be 4-hydroxy-6-methoxy-coumaranone (XI *b*) showing that there has been besides coumaranone formation partial demethylation in the susceptible 4-position.



A similar behaviour is noticed with gossypetol-tetramethyl-ether (XII *a*) which forms 4-hydroxy-6: 7-dimethoxy-coumaranone (XIII *a*) and calycopteretol-pentamethyl-ether (XII *b*) which gives rise to 4-hydroxy 5: 6: 7-trimethoxy-coumaranone (XIII *b*). The 4-position in these coumaranones corresponds to the 5-position in flavones and flavonols and due to the influence of the neighbouring carbonyl group it suffers easy demethylation. The hydroxyl in this position is again resistant to methylation owing to the existence of chelation.

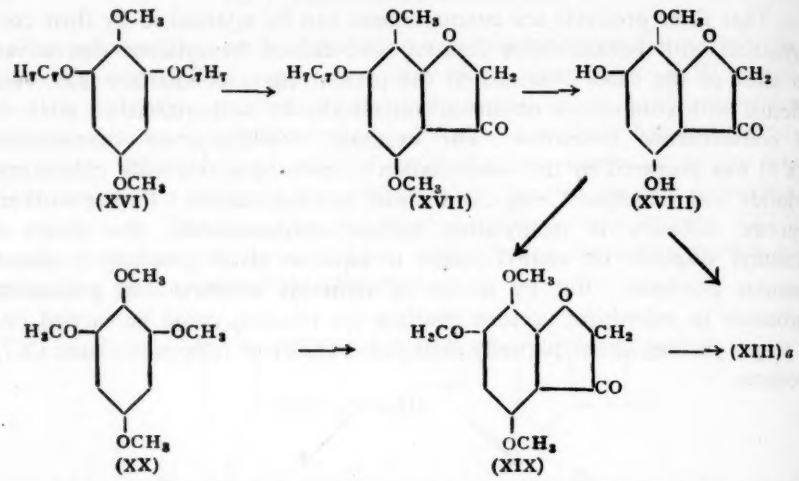


That these products are coumaranones can be established by their condensation with benzaldehyde forming well-defined benzylidene derivatives. In most of the cases obtained in the present study comparison has been effected with compounds obtained synthetically by well-established methods of coumaranone formation. For example, 4: 6-dihydroxy coumaranone (IX *b*) was prepared by the condensation of phloroglucinol with chloracetyl chloride and subsequent ring closure with sodium acetate. Earlier workers reported difficulty in methylating hydroxy-coumaranones. The action of dimethyl sulphate or methyl iodide in aqueous alkali generally produced resinous products. But by means of dimethyl sulphate and potassium carbonate in anhydrous acetone medium the reaction could be carried out in stages yielding either partially methylated (XIV) or fully methylated (XV) products.

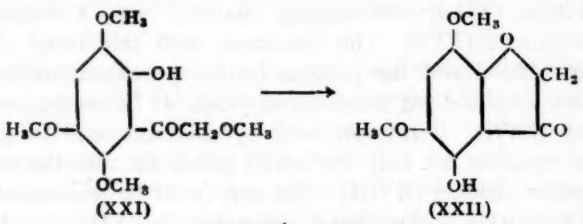


For the synthesis of coumaranone (XIII *a*) obtained from gossypetol-tetramethyl-ether (XII *a*) the starting material was 1: 4-dimethoxy-2: 6-dibenzyloxy-benzene (XVI). This condenses with chloracetyl chloride with partial debenzylation and the product (ortho-hydroxy-chloroketone) subsequently reacts with sodium acetate and yields 4: 7-dimethoxy-6-benzyloxy-coumaranone (XVII). Treatment with hydrobromic acid in glacial acetic acid solution removes not only the benzyl group but also the methyl group in the 4-position yielding (XVIII). But this could be remethylated partially to form 4-hydroxy-6: 7-dimethoxy coumaranone (XIII *a*) and completely to produce 4: 6: 7-trimethoxy-coumaranone (XIX). In this connection it may be stated that 1: 2: 3: 5-tetramethoxy-benzene (XX) undergoes this condensation with chloracetyl chloride in the cold rather poorly and only low yields of 4: 6: 7-trimethoxy coumaranone (XIX) could be obtained by further treatment with sodium acetate. This when demethylated with hydrobromic acid formed the dimethyl ether (XIII *a*) with the 4-hydroxyl group free.

An important case where a definite proof that it was a flavonol was needed at an earlier date was gardenin. Its constitution has recently been



conclusively established as 5-hydroxy-3 : 6 : 8 : 3′ : 4′ : 5′-hexamethoxy-flavone by synthetic methods.[4] The ketonic fission product (XXI) of methyl gardenin is now shown to undergo coumaranone conversion with hydrobromic acid. Here again the coumaranone has a methoxyl group less due to partial demethylation affecting position 4 and it is therefore considered to be 4-hydroxy-5 : 7-dimethoxy-coumaran-3-one (XXII). In conformity with this constitution it gives a marked colour with ferric chloride.



Experimental

6-*Hydroxy-coumaran*-3-*one* (*IX a*)

ω-Methoxy-resacetophenone (1·0 g.) was treated with an aqueous solution of hydrobromic acid (20 c.c.; 40%). The mixture was heated at 100° over a boiling water-bath for 3 hours. It was filtered through cotton-wool to remove uncrystallisable resinous matter that separated out during the reaction. The clear aqueous solution was left in the refrigerator for 48 hours. Since nothing separated out, it was extracted with ether and the ether solution concentrated when a brown solid was obtained. It crystallised

from aqueous alcohol as pale yellow rectangular plates melting at 239–40°. Yield, 0·1 g. (Found: C, 63·7; H, 4·3; $C_8H_6O_3$ requires C, 64·0; H, 4·0%.)

By heating it at 60° with concentrated sulphuric acid and benzaldehyde it gave the benzal derivative which crystallised from alcohol as pale yellow prisms melting at 261–62°. This gave a blood-red colour with concentrated sulphuric acid.

For purposes of comparison 6-hydroxy-coumaranone was prepared according to the procedure of Arima and Okamato[5] with modifications. To an ice-cooled solution of resorcinol (11·0 g., 1 mol.) in dry ether (50 c.c.) anhydrous aluminium chloride (40 g., 3 mols.) was added in small lots followed by chloracetyl chloride (8 c.c., 1 mol.) in drops and the mixture was allowed to stand overnight. Water and hydrochloric acid were added carefully and the ether was driven off over a hot water-bath. The heating was continued for a further 15 minutes and the mixture cooled. The solid that separated out was filtered and boiled with a 10% aqueous solution of sodium acetate. On cooling the resulting solution, a yellow solid was obtained. It crystallised from alcohol as yellow rectangular plates melting at 239–40° and gave a benzylidene derivative melting at 261–62°.

There was complete identity between the two sets of samples and the mixed melting points were undepressed.

6-*Methoxy-coumaran*-3-*one* (*XI a*)

(*a*) ω: 4-Dimethoxy-2-hydroxy-acetophenone (1·0 g) was treated with hydrobromic acid (20 c.c.; 40%). The reaction was carried out and the product worked up as in a previous experiment. It crystallised from alcohol as straw-coloured needles melting at 119–20°. Yield, 0·1 g. (Found: C, 66·2; H, 5·0; $C_9H_8O_3$ requires C, 65·9; H, 4·9%.) It did not give any colour with alcoholic ferric chloride and was insoluble in aqueous alkali.

(*b*) 6-Hydroxy-coumaranone was methylated using excess of dimethyl sulphate and anhydrous potassium carbonate in dry acetone medium. The product was found to be identical with the above sample.

(*c*) 6-Methoxy-coumaranone was also prepared by modification of the method of Blom and Tambor[6] using monomethyl resorcinol and chloracetyl chloride and dry ether. The earlier authors used bromacetyl bromide and carbon disulphide. The product agreed with the sample described above and with the description of Blom and Tambor.

4: 6-*Dihydroxy-coumaran*-3-*one* (*IX b*)

(*a*) ω-Methoxy-phloracetophenone (1·0 g.) was heated with hydrobromic acid (20 c.c.; 40%) for 3 hours at 100°. After filtering the reaction mixture through cotton, the clear filtrate was left in the refrigerator for 48 hours. The yellow solid that separated out crystallised from hot water as pale yellow rectangular plates melting at 248–49°. Yield, 0·1 g. (Found: C, 57·6; H, 3·9; $C_8H_6O_4$ requires C, 57·8; H, 3·6%.)

With alcoholic ferric chloride it gave a purple colour and was soluble in aqueous alkali. When heated with benzaldehyde and concentrated sulphuric acid it gave the benzylidene derivative which melted at 297–98°.

(*b*) The dihydroxy-coumaranone was also prepared from phloroglucinol by condensation with chloracetyl chloride and dry ether and subsequent treatment of the ω-chloroketone with sodium acetate. It melted at 248–49° and was identical with the sample described under (*a*). The mixed melting point was also undepressed. This substance was prepared earlier by Slater and Stephen[7] by the condensation of phloroglucinol with hydroxy-acetonitrile. The older and the present descriptions of the compound are in agreement.

4-*Hydroxy*-6-*methoxy-coumaran*-3-*one* (*XI b*)

(*a*) ω: 4: 6-Trimethoxy-2-hydroxy-acetophenone (1·0 g.) was heated with hydrobromic acid (20 c.c.; 40%). The product crystallised from alcohol as colourless needles melting at 147–48°. Yield, 0·1 g. (Found: C, 60·4; H, 4·6; OCH_3, 17·6; $C_9H_8O_4$ requires C, 60·0; H, 4·4; OCH_3, 17·2%.)

With alcoholic ferric chloride it gave a brown colour and was sparingly soluble in aqueous alkali though the solution was coloured yellow.

(*b*) The above coumaranone was also obtained by the partial methylation of 4: 6-dihydroxy-coumaranone (IX *b*) using the requisite quantity of dimethyl sulphate and anhydrous potassium carbonate in dry acetone medium and boiling for 6 hours only.

4: 6-*Dimethoxy-coumaranone* (*XV*)

4: 6-Dihydroxy-coumaranone (IX *b*) (1·7 g.) was boiled with dimethyl sulphate (4·0 c.c.) and anhydrous potassium carbonate (10 g.) in dry acetone medium (50 c.c.) for 30 hours. The dimethyl ether crystallised from alcohol as rectangular plates and prisms melting at 101–02°. (Found: C, 62·2; H, 5·3; $C_{10}H_{10}O_4$ requires C, 61·9; H, 5·2%.) With alcoholic ferric chloride it did not give any colour and was insoluble in aqueous alkali.

4-Hydroxy-6: 7-dimethoxy-coumaranone (XIII a)

First method.—Gossypetol-tetramethyl ether[8] (1·0 g.) obtained by the fission of hexamethyl-gossypetin was heated at 100° for 3 hours with hydrobromic acid (20 c.c.; 40%) and the product worked up as in similar cases. It crystallised from aqueous alcohol as colourless rectangular plates melting at 138–39°. Yield, 0·1 g. (Found: C, 57·5; H, 5·1; OCH_3, 29·9; $C_{10}H_{10}O_5$ requires C, 57·2; H, 4·9; OCH_3, 29·5%.) With alcoholic ferric chloride it gave a brown colour and was sparingly soluble in aqueous alkali.

Second method.—

4: 7-Dimethoxy-6-benzyloxy-coumaranone (XVII)

To an ice-cold dry ether solution of 2: 6-dibenzyloxy-1: 4-dimethoxy benzene[9] (7·0 g.) anhydrous aluminium chloride (7·5 g.) was added in small lots and chloracetyl chloride (1·5 c.c.) drop by drop. After 2 hours, water (100 c.c.) and concentrated hydrochloric acid (50 c.c.) were added carefully. Ether was distilled off and the mixture was heated at 100° over a boiling water-bath for 15 minutes. On cooling the ω-chloroketone separated out as a dark coloured semi-solid. It was treated with an aqueous solution (10%, 100 c.c.) of sodium acetate and the mixture was heated on a water bath for one hour. The product crystallised from alcohol as grey prisms melting at 153–54°. (Found: C, 68·0; H, 5·9; $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·5%.) With alcoholic ferric chloride it did not give any colour and was insoluble in aqueous alkali.

4: 6-Dihydroxy-7-methoxy-coumaranone (XVIII)

The above dimethoxy-benzyloxy-coumaranone (0·8 g.) was treated with a mixture of glacial acetic acid (5·0 c.c.) and a solution of hydrobromic acid in glacial acetic acid (5·0 c.c., 60%). The mixture was heated at 100° over a water-bath for one hour. On cooling and diluting the solution with water a dark coloured solid separated out. It crystallised from alcohol as pale brown prisms melting at 251–52°. (Found: C, 55·5; H, 3·5; $C_9H_8O_5$ requires C, 55·1; H, 3·3%.) With alcoholic ferric chloride it gave a brown colour and was easily soluble in aqueous alkali.

4-Hydroxy-6: 7-dimethoxy-coumaranone (XIII a)

The above dihydroxy compound (0·2 g.) was methylated using dimethyl sulphate (0·1 c.c.) and anhydrous potassium carbonate (5·0 g.) in dry acetone medium (20 c.c.) and boiling for 6 hours. The partial methyl ether crystallised from alcohol as colourless rectangular plates melting at 138–39°. Mixed

melting point with the compound obtained by the first method was undepressed.

Third method.—1 : 2 : 3 : 5-Tetramethoxy-benzene and chloracetyl chloride were condensed together in dry ether medium in the presence of aluminium chloride and the product worked up and treated with sodium acetate as in a similar reaction described above. 4 : 6 : 7-Trimethoxy coumaranone (XIX) was first obtained as a viscous liquid; this liquid was also obtained by the complete methylation of (XVIII). It was subjected to partial demethylation using hydrobromic acid in glacial acetic acid medium according to the procedure described previously. The demethylated compound, 4-hydroxy-6 : 7-dimethoxy-coumaranone melted at 138–39° and the mixed melting point with the compound obtained by the first method was undepressed.

4-*Hydroxy*-5 : 6 : 7-*trimethoxy-coumaranone* (*XIII b*)

Calycopteretol-pentamethyl ether[10] (XII *b*) (1·0 g.) obtained from hexamethyl-calycopterin was heated for 3 hours at 100° with hydrobromic acid (20 c.c.; 40%). The coumaranone crystallised from alcohol as colour, less rectangular prisms melting at 126–27°. Yield, 0·1 g. (Found: C, 55·2; H, 4·8; OCH_3, 38·9; $C_{11}H_{12}O_6$ requires C, 55·0; H, 5·0; OCH_3, 38·8%.) With alcoholic ferric chloride it gave a brown colour and was sparingly soluble in aqueous alkali.

4-*Hydroxy*-5 : 7-*dimethoxy-coumaranone* (*XXII*)

2-Hydroxy-ω : 3 : 5 : 6-tetramethoxy-acetophenone[4] (XXI) was prepared by the alkali fission of methyl gardenin. The ketone (1·5 g.) was heated with an aqueous solution of hydrobromic acid (50 c.c.; 40%). After cooling, the mixture was extracted with ether and the ether solution dried over sodium sulphate. When the solvent was removed by evaporation, a semi-solid was left behind. It crystallised from petroleum ether as very pale grey flakes melting at 51–52°. Yield, 0·2 g. (Found: OCH_3, 30·0; $C_{10}H_{10}O_5$ requires OCH_3, 29·5%.) With alcoholic ferric chloride it gave a green colour and it was sparingly soluble in aqueous alkali. Its benzylidene derivative crystallised from alcohol as yellowish brown tiny prisms and melted at 183–4°.

Summary

A method of distinguishing between a flavone and a flavonol and characterising the latter is described. It consists in subjecting the ketonic fission product of the fully methylated anthoxanthin, representing the condensed benzene nucleus to the action of 40% aqueous hydrobromic acid,

ω-Methoxy-ketones derived from flavonols yield coumaranones which could be converted into benzylidene derivatives. Simpler examples and more difficult cases such as gossypetol-tetramethyl-ether and calycopteretol pentamethyl-ether have been used for the investigation. The nature of the products has been proved by independent synthesis. The ketone obtained by the fission of methyl gardenin undergoes this reaction and hence supports the constitution of gardenin as a flavonol. Ortho-hydroxy-ketones which are unsubstituted in the ω-position do not yield any crystallisable product in this reaction.

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SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

Part X. Synthesis of Carthamidin and Iso-Carthamidin

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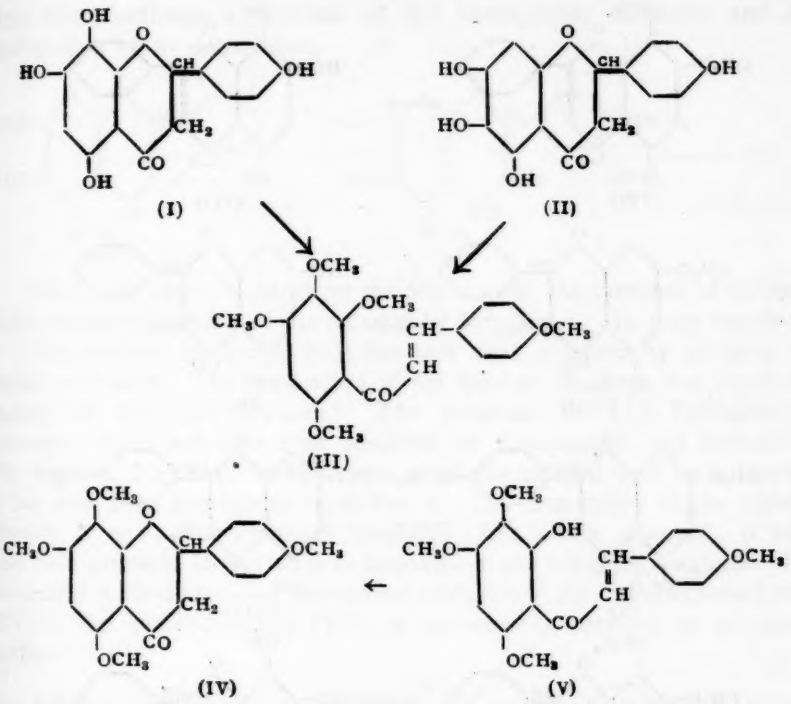
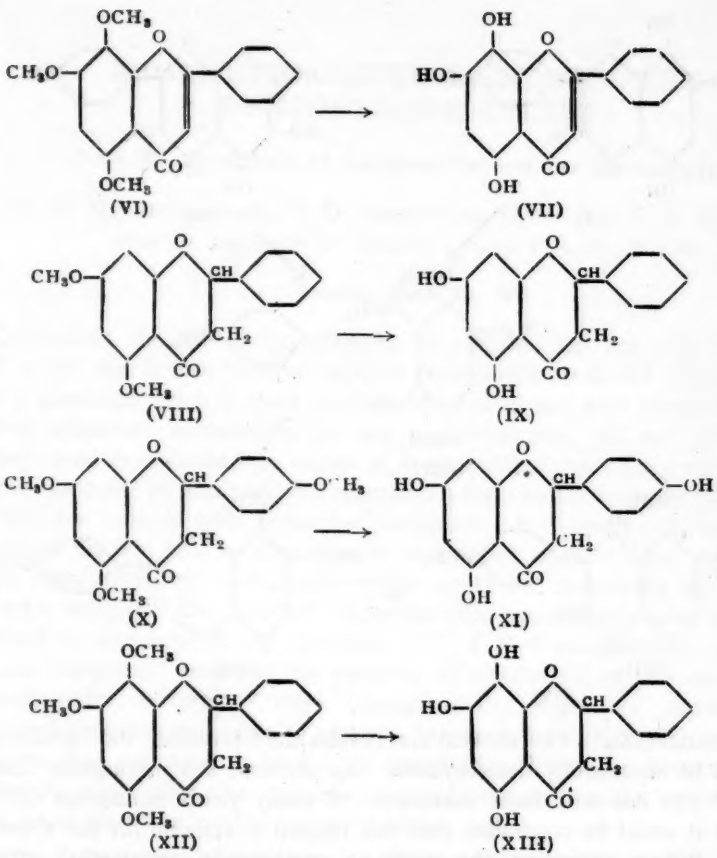
Received March 28, 1949

Carthamin, the red colouring matter of safflower has not only been used as a dye but is also believed to have remarkable medicinal properties. It is a glucoside which is most conveniently hydrolysed with phosphoric acid. Two aglucones carthamidin (I) and iso-carthamidin (II) are formed and they could be separated by means of moist chloroform. They were investigated in detail by Kuroda[1] who represented them by the formulæ (I) and (II). They are isomers with distinctive properties. In support of these constitutions she was able to show that by acetylation both of them gave rise to the same β-acetyl carthamidin which could be methylated by Freudenberg's method. The product, β-carthamidin pentamethyl ether (III), was found to be identical with synthetic 2:3:4:6:4′-pentamethoxy chalkone. Later Bargellini[2] described the synthesis of what could be considered to be carthamidin tetramethyl ether (flavanone IV) from the corresponding chalkone tetramethyl ether (V) by ring closure. Its relationship to carthamidin does not seem to have been established. There has been no report that this tetramethyl ether could be prepared from carthamidin by methylation or could be demethylated to carthamidin.

In earlier publications[3] from this laboratory the use of anhydrous aluminium chloride in nitrobenzene solution for the partial demethylation of flavanones and chalkones has been described. Hydrobromic acid is also suitable for this purpose but it brings about loss by excessive resinification. In attempts to effect complete demethylation, hydriodic acid is found to be unsatisfactory since it seems to produce some other ununderstood complicated changes besides demethylation. This reaction is being investigated separately. The use of anhydrous aluminium chloride in benzene solution seemed to offer better chances of success. Successful use of it was made in the demethylation of wogonin dimethyl ether (VI) to norwogonin[4] (VII). A more relevant example for the present purpose is the demethylation of the 5:7-dimethoxy flavanone (VIII) to the corresponding dihydroxy



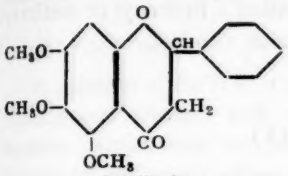
compound (IX).[5] This showed that besides the 5-position, the 7-position also could be successfully demethylated. As the next step naringenin trimethyl ether[5] (X) has now been examined. It easily yields naringenin (XI) and hence it could be concluded that this reagent is suitable for the 4′-position also. Before extending the work to carthamidin tetramethyl ether the simpler case of 5:7:8-trimethoxy flavanone (XII) was taken up. It also underwent smooth demethylation yielding a product which had all the properties that could be expected for 5:7:8-trihydroxy flavanone (XIII). When a similar product was obtained from 5:7:8:4′-tetramethoxy flavanone (IV) it could safely be considered to be the corresponding 5:7:8:4′-tetrahydroxy flavanone (I). Its properties and reactions closely agreed with those already recorded in the literature for carthamidin.[1] Though it has not been possible for us so far to secure a genuine sample of carthamin paste and isolate carthamidin from it or secure an authentic sample from Miss Kuroda, the agreement is so close that it could be safely stated that the synthesis of carthamidin has now been effected and that it supports the constitution given for it by Kuroda.

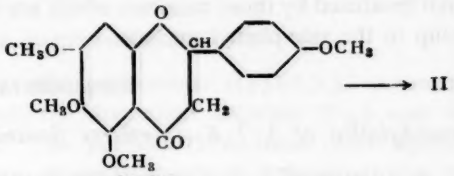


That no isomeric change takes place during the above demethylation to carthamidin is confirmed by the methylation of the product with 4 moles of dimethyl sulphate and anhydrous potassium carbonate in acetone medium. This method of methylation eliminates the difficulties experienced by previous workers. In the present case the product is a chalkone tetramethyl ether (V) which could be subsequently cyclised to carthamidin tetramethyl ether (IV). The course of the reaction is in agreement with similar cases reported recently.[5]

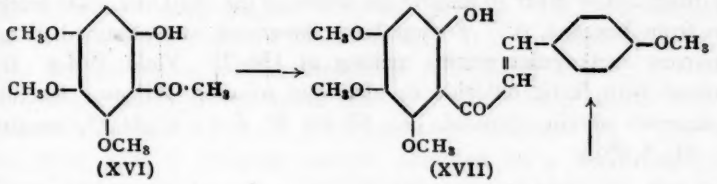
The above experimental technique has been further extended to the demethylation of 5:6:7-trimethoxy flavanone (XIV) and 5:6:7:4′-tetramethoxy flavanone (XV). Both get completely demethylated. The product from the latter agreed very closely in its properties with isocarthamidin (II),

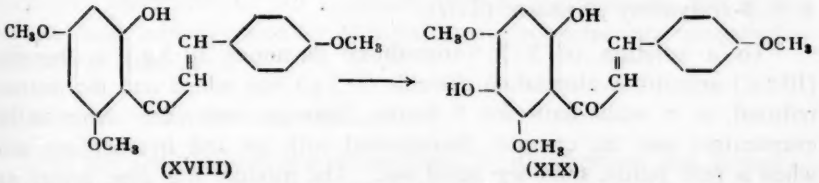
Thus this constitutes a synthesis of this tetrahydroxy flavanone and a confirmation of its constitution.


(XIV)


(XV)

Among the ethers required for the above work, the synthesis of carthamidin tetramethyl ether (IV) was reported by Bargellini.[2] The lower member, 5:7:8-trimethoxy flavanone (XII) has now been prepared by adopting a similar procedure. The preparation of the required chalkone was reported recently by Rao and Seshadri.[6] The synthesis of 5:6:7-trimethoxy flavanone (XIV) has also been described by Rajagopalan and Seshadri.[7] The required 2-hydroxy-chalkone was originally isolated only as a liquid. It has now been possible to crystallise it. The preparation of the higher member, 5:6:7:4′-tetramethoxy flavanone (XV) is now reported. It has now been prepared in two ways as indicated in the following diagrams. In the second method involving persulphate oxidation of the 2-hydroxy-chalkone (XVIII), the quinol-chalkone (XIX) is conveniently obtained as an intermediate.


(XVI) (XVII)


(XVIII) (XIX)

In the reactions of the flavanones studied in the course of this work two points require special mention. (1) Bargellini's test with sodium amalgam which is characterised by the formation of green flocs in the case of 5:6:7-hydroxy flavones like baicalein, scutellarein, quercetagetin and other members of the series, produces only a green solution followed by a brown precipitate in the case of the corresponding flavanones. (2) The

bright red colour or a related shade which is readily given by most flavanones when treated with magnesium and hydrochloric acid in alcoholic solution is not produced by those members which are devoid of a hydroxyl or methoxyl group in the side-phenyl nucleus.

Experimental

Demethylation of 5:7:4′-*trimethoxy flavanone* (*X*)

A solution of 5:7:4′-trimethoxy flavanone (0·5 g.) in benzene (10 c.c.) was refluxed with anhydrous aluminium chloride (2 g.) for 2 hours. Benzene was then distilled off and the complex decomposed with ice and hydrochloric acid. The solid that separated was filtered and washed with ice-cold hydrochloric acid. It crystallised from dilute alcohol in the form of short needles melting at 244–45° alone or in admixture with an authentic sample of naringenin (XI).

5:7:8-*Trimethoxy flavanone* (*XII*)

A solution of 2-hydroxy 3:4:6-trimethoxy chalkone[6] (1 g.) in alcoholic sulphuric acid (100 c.c., 4%) was refluxed on a water-bath for 24 hours. It was concentrated to 20 c.c. when the unreacted chalkone separated out. This was then filtered and the filtrate diluted with an equal volume of water when a colourless solid crystallised out. It was filtered and washed with small quantities of ether to remove the traces of the chalkone. On recrystallisation from benzene, 5:7:8-trimethoxy flavanone was obtained as colourless narrow rectangular prisms melting at 156–7°. Yield, 0·4 g. It gave no colour with ferric chloride in alcoholic solution and was insoluble in cold aqueous alkali. (Found: C, 68·4; H, 6·1; $C_{18}H_{18}O_5$ requires C, 68·7; H, 5·8%.)

5:7:8-*Trihydroxy flavanone* (*XIII*)

To a solution of 5:7:8-trimethoxy flavanone (0·5 g.) in benzene (10 c.c.) anhydrous aluminium chloride (1·5 g.) was added and the mixture refluxed on a water-bath for 2 hours. Benzene was then removed by evaporation and the complex decomposed with ice and hydrochloric acid when a pale yellow solid separated out. The mixture was then heated on a water-bath for a few minutes to complete the decomposition and after cooling was extracted with ether. On evaporating the ether solution a pale yellow solid was obtained. It crystallised from ethyl acetate-benzene mixture in the form of pale yellow prisms melting at 208–10°. It gave a dark reddish brown colour with ferric chloride in alcoholic solution and with *p*-benzoquinone gave a reddish brown colouration. Yield, 0·25 g.

(Found: C, 66·0; H, 4·6; $C_{15}H_{12}O_5$ requires C, 66·2; H, 4·4%.) It did not give any red colour with magnesium and hydrochloric acid, but in all other reactions it very closely resembled carthamidin.

5:7:8:4′-*Tetrahydroxy flavanone* (*carthamidin*) (*I*)

A solution of 5:7:8:4′-tetramethoxy flavanone[2] (IV) (0·5 g.) in benzene (10 c.c.) was treated with anhydrous aluminium chloride (2 g.) and the reaction carried out as before. The product crystallised from aqueous chloroform as pale yellow broad rectangular prisms melting at 216–18°. It dissolved in aqueous alkali (2 N) to give a blue colour changing to reddish brown. Its alcoholic solution gave (1) with a drop of ferric chloride a green colouration changing rapidly to reddish brown, (2) with magnesium and hydrochloric acid a magenta colour, (3) a deep blue colour with aqueous barium hydroxide and (4) with lead acetate a yellow precipitate changing to green. Thus it agreed with carthamidin in all its properties. Yield, 0·2 g. (Found: C, 55·1; H, 5·2; $C_{15}H_{12}O_6$, $2H_2O$ requires C, 55·5; H, 5·0%.)

Methylation

Carthamidin (0·2 g.) was dissolved in acetone (20 c.c.), dimethyl sulphate (0·3 c.c.; 4·4 mols.) and anhydrous potassium carbonate (1 g.) were added and the mixture refluxed on a water-bath for 8 hours. It was then filtered and the potassium salts washed with hot acetone. On evaporating the acetone solution a bright yellow solid was left. It crystallised from alcohol as bright orange yellow rectangular plates and prisms melting at 144–5°. It gave a deep reddish brown colour with ferric chloride in alcohol and was identical with 2-hydroxy-3:4:6:4′-tetramethoxy chalkone (V). The mixed melting point with a synthetic sample obtained from 2-hydroxy-3:4:6-trimethoxy acetophenone and anisaldehyde[2] was undepressed. On boiling with alcoholic sulphuric acid for 24 hours it was converted into carthamidin-tetramethyl ether (IV).

2-*Hydroxy*-4:5:6-*trimethoxy chalkone*

This was first prepared as a viscous liquid by Rajagopalan and Seshadri.[7] When a concentrated alcoholic solution is allowed to stay in the refrigerator for two days it comes out as a crystalline solid. Recrystallisation from alcohol yields yellow broad rectangular plates melting at 132–3°. It gives a deep reddish brown colour with ferric chloride in alcohol. (Found: C, 69·0; H, 5·6; $C_{18}H_{18}O_5$ requires C, 68·7; H, 5·8%). It could be cyclised into 5 : 6 : 7-trimethoxy flavanone, m.p. 154–55° (XIV).

5: 6: 7-*Trihydroxy flavanone*

5: 6: 7-Trimethoxy flavanone (XIV) (0·2 g.) was refluxed in benzene solution with anhydrous aluminium chloride (1 g.) for 2 hours and the product worked up. It crystallised from benzene-chloroform mixture as colourless tiny prisms melting at 226–27°; yield 0·1 g. It was easily soluble in alcohol, less in benzene and insoluble in chloroform. It gave a deep brown colour with ferric chloride in alcohol. It dissolved in aqueous sodium hydroxide forming a green solution which rapidly changed to yellow. Barium hydroxide gave a similar green solution. An alcoholic solution of the substance produced a deep green colour with sodium amalgam; this rapidly changed to brown and finally a brown precipitate was formed. Lead acetate in methyl alcoholic solution gave a green precipitate. (Found: C, 66·4; H, 4·0; $C_{15}H_{12}O_5$ requires C, 66·2; H, 4·4%.) This substance resembled closely in its colour reaction isocarthamidin except in the lack of red colour when treated with magnesium and hydrochloric acid in alcoholic solution.

2-*Hydroxy*-4 : 5: 6: 4′-*tetramethoxy chalkone* (*XVII*)

2-Hydroxy-4: 5: 6-trimethoxy acetophenone[8] (2 g.) was dissolved in alcohol (50 c.c.) and anisaldehyde (4 g.) added. A solution of potassium hydroxide (5 g.) in water (10 c.c.) was then introduced during the course of fifteen minutes, the temperature being maintained below 5°. The reaction was allowed to proceed at the laboratory temperature for 4 days, the solution being kept out of contact with air. The mixture was then diluted with water (100 c.c.) and extracted twice with ether to remove any unreacted aldehyde. The solution was then acidified while cooling under the tap when the hydroxy chalkone was precipitated as a slightly sticky reddish brown solid. It was collected, washed and taken up in ether. The ether solution was washed with dilute aqueous sodium carbonate to remove anisic acid. Distillation of ether yielded the chalkone as an orange yellow crystalline solid. Yield 1·5 g. On recrystallisation from alcohol it was obtained as deep yellow elongated rhombohedrons and melted at 141–42°. It was moderately soluble in alcohol and ether and dissolved more readily in acetone. It dissolved in aqueous sodium hydroxide with an yellow colour and gave a reddish brown colouration with ferric chloride in alcoholic solution. Its alcoholic solution developed no colour with magnesium and hydrochloric acid. (Found: C, 66·4; H, 5·7; $C_{19}H_{20}O_6$ requires, C, 66·3; H, 5·8%.)

2: 5-*Dihydroxy*-4: 6: 4′-*trimethoxy chalkone* (*XIX*)

2-Hydroxy-4: 6: 4′-trimethoxy chalkone (XVIII)[9] (1 g.) was dissolved in a solution of sodium hydroxide (2 g. in 25 c.c. water). The solution was

cooled to 15–20° and kept continually stirred. A solution of potassium persulphate (1·5 g.) in water (40 c.c.) was introduced dropwise during the course of 2 hours, the temperature being maintained at 15–20° throughout the reaction. After allowing to stand for 24 hours the dark brown reaction mixture was rendered distinctly acid to litmus by adding concentrated hydrochloric acid. The recovered unreacted chalkone was filtered and the filtrate extracted twice with ether. The clear solution was treated with sodium sulphite (1 g.) and concentrated hydrochloric acid (20 c.c.) and heated on a boiling water-bath for ½ hour. On cooling under the tap a reddish yellow crystalline mass of the oxidation product separated. It was filtered and washed with water; some more of it was obtained by extracting the filtrate with ether. The dihydroxy-trimethoxy chalkone crystallised from alcohol in red glistening prisms melting at 190–91°; yield, 0·3 g. It gave a deep reddish brown colour with ferric chloride in alcoholic solution and dissolved in aqueous alkali forming a deep red solution. (Found: C, 66·0; H, 5·5; $C_{18}H_{18}O_6$ requires C, 65·5; H, 5·6%.)

Partial methylation

The above dihydroxy chalkone (XIX) (0·2 g.) was methylated by boiling with dimethyl sulphate (0·1 c.c.) and anhydrous potassium carbonate (0·5 g.) in dry acetone (15 c.c.) for 6 hours. It was filtered and the potassium salts washed with acetone. On distilling off acetone a yellow crystalline solid was obtained. It crystallised from alcohol as elongated rhombohedrons and melted at 141–42°. It was soluble in cold aqueous sodium hydroxide and gave reddish brown colour with alcoholic ferric chloride. The mixed melting point with the sample of 2-hydroxy-4: 5: 6: 4′-tetramethoxy chalkone (XVII) described above was undepressed.

5: 6: 7: 4′-*Tetramethoxy flavanone* (*Isocarthamidin tetramethyl ether*) (*XV*)

The hydroxy-tetramethoxy chalkone (XVII) (1 g.) was refluxed for 24 hours with alcoholic sulphuric acid (100 c.c.; 4%). The solution was concentrated under reduced pressure to 10 c.c. and the unreacted chalkone that separated on cooling filtered. The filtrate was diluted with an equal volume of water and left overnight. The colourless crystalline solid now produced was filtered and crystallised from dilute alcohol. Yield, 0·3 g. The tetramethoxy flavanone was obtained as colourless rhombohedral prisms melting at 124–25°. It was insoluble in cold dilute alkali and gave no colour with ferric chloride in alcoholic solution. With magnesium and concentrated hydrochloric acid its alcoholic solution developed a red colour. (Found: C, 66·2; H, 6·0; $C_{19}H_{20}O_6$ requires C, 66·3; H, 5·8%)

5 : 6 : 7 : 4′-*Tetrahydroxy flavanone* (*Isocarthamidin*) (*II*)

As in the previous cases the tetramethoxy flavanone (XV) (0·5 g.) was dissolved in benzene, treated with anhydrous aluminium chloride (2 g.), refluxed on a water-bath for 2 hours and the product worked up. It was first crystallised from acetone chloroform mixture and then from dilute methyl alcohol when it was obtained in the form of yellow prisms melting at 239–40° (Kuroda gave m.p. 240°); yield 0·2 g. It gave a deep brown colour when rubbed with aqueous alkali (2 N). Its alcoholic solution gave (1) a bluish green colour changing to reddish brown with ferric chloride, (2) a magenta colour when reduced with magnesium and hydrochloric acid, (3) a green colour with aqueous barium hydroxide, (4) a green precipitate with lead acetate and (5) with sodium amalgam a green colour fading rapidly with the formation of a brown precipitate. Thus the product agreed in all its properties with isocarthamidin described by Kuroda.[1] (Found: C, 62·2; H, 4·5; $C_{15}H_{12}O_6$ requires C, 62·5; H, 4·2%.)

Summary

The method of demethylation using aluminium chloride in benzene medium is shown to be applicable to polymethoxy flavanones. 5 : 7 : 4′-, 5 : 7 : 8- and 5 : 6 : 7-trimethoxy flavanones yield the corresponding trihydroxy compounds. Similarly carthamidin and isocarthamidin are obtained from their tetramethyl ethers whose synthesis is described. This work provides synthetic confirmation of the constitution of these tetrahydroxy flavanones proposed by Kuroda. That no isomeric change takes place in the preparation of carthamidin is established by its methylation to its tetramethyl ether.

References

1. Kuroda .. *J. C. S.*, 1930, 752 and 765.
2. Bargellini .. *Br. Chem. Abs.*, 1940, A, ii, 186.
3. Rao and Seshadri .. *Proc. Ind. Acad. Sci.* A, 1946, **23**, 213.
   Narasimhachari and Seshadri .. *Ibid.*, 1949, **29**, 265.
4. Sastri and Seshadri .. *Ibid.*, 1946, **24**, 251.
5. Narasimhachari and Seshadri .. *Ibid.*, 1948, **27**, 223.
6. Rao and Seshadri .. *Ibid.*, 1948, 27, 385.
7. Rajagopalan and Seshadri .. *Ibid.*, 1948, **27**, 85.
8. Sastri and Seshadri .. *Ibid.*, 1946, **23**, 262.
9. Kostanecki and Tambor .. *Ber.*, 1904, 792.

STUDIES ON THE DEPENDENCE OF OPTICAL ACTIVITY ON CHEMICAL CONSTITUTION

Part XXXII. The Rotatory Dispersion of *a*- and β-Naphthyl-imino- and amino-Camphors (*d*- and *dl*-)

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THE present investigation is in continuation of the earlier work described in Parts I and II of the series[1]. Singh and collaborators determined the rotatory power of α- and β-naphthyl-imino- and amino-*d*-camphors in two solvents for the sodium *D*-line only. In the present case the investigation has been extended to the whole range of the visible spectrum for 6 solvents. The racemic forms of these compounds are also described and their nature studied.

NATURE OF THE ROTATORY DISPERSION

The rotatory dispersion has been determined in the visible region of the spectrum (6708 Å.U. to 4358 Å.U.) for six wavelengths for the yellow coloured α- and β-naphthyliminocamphors and for twelve wavelengths in the case of colourless α- and β-naphthylaminocamphors (Tables II to V). It is found to be simple as it obeys the one-term Drude's Equation, $[\alpha] = \frac{k_0}{\lambda^2 - \lambda_0^2}$. In this equation, k, the rotation constant, may be taken as a measure of the absolute rotation for the wavelength λ for which $\lambda^2 - \lambda_0^2 = 1$. The absolute rotation constants (k_0) are thus numerically but not dimensionally identical with the magnitude of $[\alpha]$. Comparisons of rotatory power and rotation constant at the wavelength λ where $\lambda = \sqrt{1 + \lambda_0^2}$ may be regarded as those for corresponding conditions of wavelengths in which the effects of dispersion are eliminated.

The graphical method of plotting $\frac{1}{\alpha}$ against λ^2 is also applied and a straight line is obtained in all cases. Two such graphs are given in illustration (Figs. 1 and 2).

NATURE OF THE RACEMIC MODIFICATION

The melting points of the racemic forms of the β-naphthyl-imino- and -amino-camphor are higher than those of their corresponding optical isomers. They are, therefore, true *dl*-compounds. The melting points of

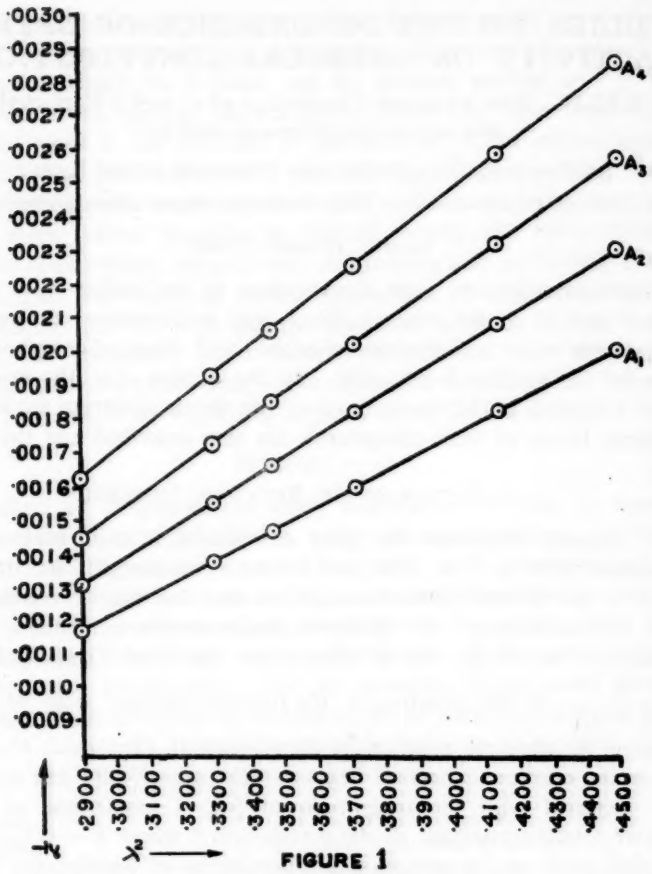


FIG. 1. A_1:—β-naphthylimino-*d*-camphor (chloroform)
A_2:—α-naphthylimino-*d*-camphor (chloroform)
A_3:—β-naphthylimino-*d*-camphor (methyl alcohol)
A_4:—α-naphthylimino-*d*-camphor (methyl alcohol)

the racemic forms of α-naphthyl-imino- and -amino-camphors are lower than those of their optical isomers. That these racemic forms are also true *dl*-compounds was determined in the following way: A small amount of the *d*-form was added to the corresponding racemic modification and the melting point was found to be lowered in each case. This clearly shows that these racemic substances are also true *dl*-compounds.

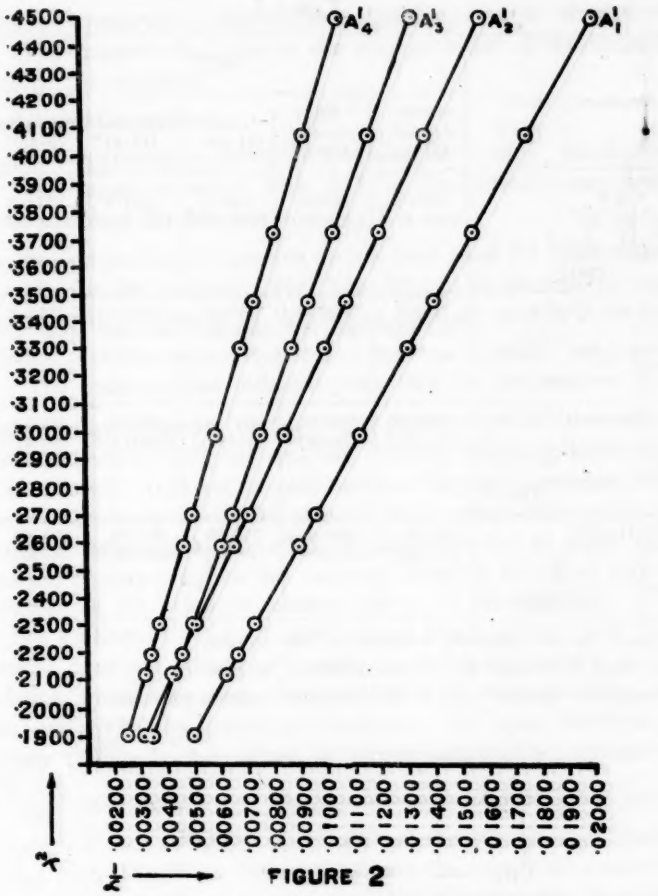
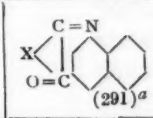
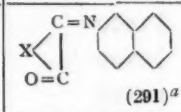
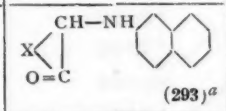
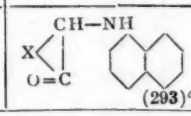


FIG. 2. A′$_1$:—α-naphthylamino-*d*-camphor (methyl alcohol)
A′$_2$:—α-naphthylamino-*d*-camphor (chloroform)
A′$_3$:—β-naphthylamino-*d*-camphor (methyl alcohol)
A′$_4$:—β-naphthylamino-*d*-camphor (chloroform)

THE EFFECT OF SOLVENT ON THE ROTATORY POWER

The molecular rotatory power $[M]_D^{32°}$ of the compounds in different solvents is given in Table I. The sequence of decreasing rotatory power is as follows:

TABLE I

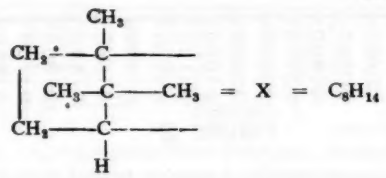
No.	Structural formula	$[M]_D^{39°}$					
		Methyl Alcohol (31·2)*	Ethyl Alcohol (25·8)*	Acetone (21·5)*	Pyridine (12·4)*	Chloroform (5·20)*	Benzene (2·28)*
1	 (291)[a]	1425·9 (345·41)[b]	1615·0 (396·05)[b]	1862·4 (446·97)[b]	1734·9 (421·27)[b]	1731·3 (410·65)[b]	1893·2 (437·37)[b]
2	 (291)[a]	1582·1 (382·66)[b]	1746·0 (395·76)[b]	1891·5 (463·85)[b]	2037·0 (455·70)[b]	1992·2 (489·75)[b]	2661·0 (504·80)[b]
3	 (293)[a]	307·65 (74·77)[b]	322·30 (78·64)[b]	410·20 (97·27)[b]	439·50 (108·17)[b]	419·34 (98·47)[b]	439·50 (108·17)[b]
4	 (293)[a]	214·24 (52·00)[b]	234·40 (56·34)[b]	266·63 (63·16)[b]	293·00 (67·71)[b]	272·00 (61·17)[b]	293·00 (72·43)[b]

* It refers to the dielectric constants of the solvent.

[a] The values in brackets refer to the molecular weights.

[b] The values in brackets refer to the molecular rotation constants,

$$K_0 = \frac{M \times k_0}{100}$$



(*a*) *α-naphthyliminocamphor*

Benzene > acetone > chloroform > pyridine > ethyl alcohol > methyl alcohol. The sequence agrees with that of the dielectric constants in the reverse order except in the case of acetone.

(*b*) *β-naphthyliminocamphor*

Benzene > pyridine > chloroform > acetone > ethyl alcohol > methyl alcohol. The sequence agrees with that of the dielectric constants in the reverse order except for pyridine.

(*c*) *α-naphthylaminocamphor*

Pyridine > benzene > chloroform > acetone > ethyl alcohol > methyl alcohol. The sequence is again in the reverse order of the dielectric constants except for pyridine.

(*d*) *β-naphthylaminocamphor*

Benzene > pyridine > chloroform > acetone > ethyl alcohol > methyl alcohol. The sequence agrees with that for the dielectric constants in the reverse order except for pyridine.

The above mentioned sequences do not hold good for other wavelengths: For example, for the mercury violet line (Hg_{4358}) in the case of α-naphthylaminocamphor the sequence of decreasing rotatory power is as follows:

Pyridine > chloroform > benzene > acetone > ethyl alcohol > methyl alcohol. The order is thus different from that for the sodium *D*-line.

It is therefore necessary for any strict comparison of the rotatory power of the compounds in different solvents that the effect of dispersion should first be eliminated. It is not an easy matter when the dispersion is complex, but when it is simple as in the case of these compounds which obey the Drude's linear relationship, the effect of dispersion can be easily eliminated. The rotation constant (k_0) of the one-term Drude's equation may be taken as a measure of the absolute rotatory power of the medium. It refers to wave length λ where $\lambda^2 - \lambda_0^2 = 1$, which is not much greater than 10,000 Å.U. The longest observed wavelength used in our measurements is Li_{6708} and extrapolation from it to near about 10,000 Å.U. is permissible in view of the linear nature of the dispersion equation. We have, therefore, included in brackets (Table I) the values of Drude's molecular rotation constant $K_C = \frac{M \times k_0}{100}$ as a measure of the absolute molecular rotatory power of the compounds. If we compare the order of these moleculer rotation constants (K_0) with $[M]_D^{32°}$ in different solvents the results are somewhat different: for example, in the case of α-naphthyliminocamphor the order of the decreasing rotatory constant (K_0) is as below:

Benzene > chloroform > acetone > pyridine > ethyl alcohol > methyl alcohol.

RELATIONSHIP BETWEEN CHEMICAL CONSTITUTION AND ROTATORY POWER

In Table I the molecular rotatory powers $[M]_D^{32°}$ of different compounds in six solvents are given. The molecular rotatory power of the β-naphthyl-imino-and-amino-camphor is higher than that of the α-naphthyl-imino-and-amino-camphor respectively. This shows that substitution in the

β-position in the naphthalene ring gives higher molecular rotatory effect than in the α-position.

It is also seen that the reduction of the naphthyl-imino-camphors to the amino derivatives causes a great fall in their rotatory power. The phenomenal depression in the rotatory power is brought about by the breaking up of the conjugation of the azethenoid group with the double bonds of the naphthalene ring (Singh and collaborators[2]).

Experimental

The derivatives of naphthyliminocamphors (*d*- and *dl*-) were prepared by the following method: Equimolecular quantities of camphorquinone (*d*- or *dl*-) and the α- or β-naphthylamine were mixed with sufficient quantity of anhydrous sodium sulphate and heated on a water-bath for several hours. When the reaction was complete, the product was poured into cold water. The yellow precipitate was repeatedly recrystallised from aqueous alcohol as fine yellow needles.

The compounds are soluble in alcohol, chloroform and methyl alcohol, less so in acetone and pyridine and insoluble in water.

The melting points of these compounds are as below:—

α-naphthyl-imino-*d*-camphor	..	M.P. 154°–55° C.
α-naphthyl-imino-*dl*-camphor	..	M.P. 143°–45° C.
β-naphthylimino-*d*-camphor	..	M.P. 143°–44° C.
β-naphthyl-imino-*dl*-camphor	..	M.P. 146°–47° C.

The α- and β-naphthyl-aminocamphors were prepared in the following way:—The corresponding naphthylimino camphor was dissolved in ether and 10% aqueous solution of potassium hydroxide and sufficient quantity of zinc dust were added in a stoppered bottle and shaken for several hours till the yellow ethereal solution become colourless. The ether layer was separated, washed with water and ether distilled off. The solid was repeatedly recrystallised from alcohol as fine colourless needles.

The compounds are soluble in pyridine, chloroform, benzene and acetone.

Their melting points are as below:

α-naphthylamino-*d*-camphor	..	M.P. 163°–64° C.
α-naphthylamino-*dl*-camphor	..	M.P. 152°–53° C.
β-naphthyl-amino-*d*-camphor	..	M.P. 153°–54° C.
β-naphthyl-amino-*dl*-camphor	..	M.P. 156°–57° C.

The rotatory power determinations were made in a 2-dcm. jacketed tube. All the observations of the rotatory power were carried out at 31°–32° C. The values of λ_0, calculated from the dispersion formulæ, are given in Tables II to V and are expressed as μ or 10^{-4} cms.

TABLE II. *α-Naphthyl-imino-camphor*

Solvent	Methyl alcohol		Ethyl alcohol		Acetone		Pyridine		Chloroform		Benzene	
Conc. g. in 100 c.c.	0·400		0·400		0·400		0·400		0·400		0·400	
Formula $\left\{\begin{matrix}[\alpha] \\ \lambda_0\end{matrix}\right.$	$\pm \frac{118{\cdot}7}{\lambda^2 - {\cdot}1049}$ 0·3239		$\pm \frac{136{\cdot}1}{\lambda^2 - {\cdot}1020}$ 0·3194		$\pm \frac{153{\cdot}6}{\lambda^2 - {\cdot}1072}$ 0·3274		$\pm \frac{145{\cdot}8}{\lambda^2 - {\cdot}1021}$ 0·3196		$\pm \frac{144{\cdot}9}{\lambda^2 - {\cdot}1091}$ 0·3304		$\pm \frac{150{\cdot}3}{\lambda^2 - {\cdot}1161}$ 0·3407	
Line	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
Li_{6708} ..	345·4	345·2	391·2	391·3	446·8	448·2	420·0	419·4	425·0	425·3	448·7	449·8
Cd_{6438} ..	383·7	383·4	Invisible		500·0	500·0	465·0	466·7	475·0	474·4	503·7	503·7
Li_{6104} ..	445·0	443·7	503·1	503·1	578·7	579·0	540·0	539·4	550·0	550·0	586·0	586·1
Na_{5893} ..	490·0	490·9	555·0	555·0	640·0	640·0	596·2	595·6	608·7	608·7	650·5	650·5
Hg_{5780} ..	518·1	518·2	586·2	586·4	677·5	677·4	625·6	628·7	645·0	644·8	690·0	689·8
Hg_{5461} ..	614·4	614·3	695·0	694·9	805·0	805·0	743·7	743·7	766·7	766·8	825·7	825·7

TABLE III. *β-Naphthyl-imino-camphor*

Solvent	Methyl alcohol		Ethyl alcohol		Acetone		Pyridine		Chloroform		Benzene	
Conc. g. in 100 c.c.	0·400		0·400		0·400		0·400		0·400		0·400	
Formula $\begin{cases}[\alpha]\\ \lambda_0\end{cases}$	$\pm\frac{131\cdot5}{\lambda^2-\cdot1053}$ 0·3245		$\pm\frac{136\cdot0}{\lambda^2-\cdot1206}$ 0·3472		$\pm\frac{142\cdot2}{\lambda^2-\cdot1284}$ 0·3584		$\pm\frac{156\cdot6}{\lambda^2-\cdot1235}$ 0·3514		$\pm\frac{168\cdot3}{\lambda^2-\cdot1001}$ 0·3164		$\pm\frac{173\cdot5}{\lambda^2-\cdot1028}$ 0·3206	
Line	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
Li_{6708} ..	381·9	381·6	412·5	413·0	442·5	442·2	480·0	479·8	480·0	481·1	500·0	500·0
Cd_{6438} ..	425·6	425·3	462·5	462·7	496·9	496·9	537·5	538·1	533·7	535·2	557·5	556·8
Li_{6104} ..	492·5	492·3	538·1	539·5	582·5	582·5	630·0	629·0	617·5	617·7	640·0	639·6
Na_{5893} ..	543·7	543·7	600·0	600·0	650·0	650·0	700·0	700·0	681·2	681·2	710·0	710·0
Hg_{5780} ..	575·0	575·0	637·5	637·2	691·9	692·0	745·0	744·0	720·0	719·4	750·0	750·6
Hg_{5461} ..	682·5	682·5	766·2	766·2	838·7	838·9	897·5	897·5	850·0	850·0	888·7	889·0

TABLE IV. *α-Naphthyl-amino-camphor*

Solvent	Methyl alcohol		Ethyl alcohol		Acetone		Pyridine		Chloroform		Benzene	
Conc. g. in 100 c.c.	0·400		0·400		0·4000		0·400		0·400		0·400	
Formula $\begin{cases}[\alpha]\\ \lambda_0\end{cases}$	$\pm\frac{17\cdot75}{\lambda^2-\cdot1015}$ 0·3186		$\pm\frac{19\cdot23}{\lambda^2-\cdot1068}$ 0·3268		$\pm\frac{21\cdot90}{\lambda^2-\cdot1065}$ 0·3264		$\pm\frac{23\cdot11}{\lambda^2-\cdot1161}$ 0·3407		$\pm\frac{20\cdot88}{\lambda^2-\cdot1226}$ 0·3501		$\pm\frac{24\cdot71}{\lambda^2-\cdot1001}$ 0·3164	
Line	Obs.	Cal.	Obs.	Cal.	Obs	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
Li_{6708} ..	51·25	51·49	56·25	56·06	63·75	63·75	69·37	69·24	63·75	63·88	70·62	70·65
Cd_{6438} ..	58·02	57·32	62·50	62·50	70·00	71·75	77·50	77·45	71·90	71·60	78·75	78·57
Li_{6104} ..	66·25	66·18	72·50	72·40	82·00	85·00	90·00	90·04	83·27	83·58	90·62	90·70
Na_{5893} ..	73·12	73·00	80·00	80·00	91·00	91·00	100·0	100·0	93·12	93·12	100·0	100·0
Hg_{5780} ..	77·50	77·14	84·37	84·65	96·25	96·25	106·2	106·0	98·75	98·81	105·6	105·6
Hg_{5461} ..	91·87	91·22	100·6	100·6	114·4	114·4	126·2	127·0	119·3	118·8	125·0	124·8
Ag_{5209} ..	105·6	105·6	116·9	116·9	133·1	132·9	148·1	148·9	140·6	140·5	144·3	144·3
Cd_{5086} ..	114·4	114·4	126·9	126·7	144·7	144·0	158·8	158·8	153·3	153·6	154·1	155·7
Cd_{4800} ..	139·4	139·2	153·1	155·7	176·9	176·9	206·0	205·8	193·7	193·9	181·2	181·9
Cd_{4678} ..	151·2	151·2	171·9	171·7	195·0	195·0	225·0	225·0	217·7	217·1	208·7	208·2
Li_{4603} ..	162·5	162·5	178·7	178·9	208·1	208·0	243·7	242·9	233·7	234·2	221·3	221·3
Hg_{4358} ..	202·5	202·5	231·2	231·2	262·5	262·5	313·7	313·7	310·0	310·0	275·0	275·0

TABLE V. *β-Naphthyl-amino-camphor*

Solvent	Methyl Alcohol		Ethyl Alcohol		Acetone		Pyridine		Chloroform		Benzene	
Conc. g. in 100 c.c.	0·400		0·400		0·400		0·400		0·400		0·400	
Formula $\begin{cases}[\alpha]\\ \lambda_0\end{cases}$	$\pm\frac{25\cdot52}{\lambda^2-\cdot1042}$ 0·3228		$\pm\frac{26\cdot84}{\lambda^2-\cdot1033}$ 0·3214		$\pm\frac{33\cdot20}{\lambda^2-\cdot1100}$ 0·3317		$\pm\frac{36\cdot92}{\lambda^2-\cdot1011}$ 0·3180		$\pm\frac{33\cdot61}{\lambda^2-0\cdot1012}$ 0·3181		$\pm\frac{36\cdot92}{\lambda^2-\cdot1011}$ 0·3180	
Line	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs	Cal.
Li_{6708} ..	73·75	73·81	79·37	77·43	97·50	97·60	106·2	105·8	91·87	92·04	106·2	105·8
Cd_{6438} ..	80·62	80·22	86·25	86·25	108·7	109·0	118·1	117·8	107·5	107·3	118·1	117·8
Li_{6104} ..	95·08	95·08	99·75	99·75	126·2	126·5	135·6	136·0	123·7	123·9	135·6	136·0
Na_{5892} ..	105·0	105·0	110·0	110·0	140·0	140·0	150·0	150·0	143·1	143·1	150·0	150·0
Hg_{5780} ..	111·2	111·0	116·2	116·2	147·6	148·1	158·7	158·5	149·4	149·4	158·7	158·5
Hg_{5461} ..	131·9	131·7	137·5	137·8	176·9	176·5	187·5	187·4	170·6	170·7	187·5	187·4
Ag_{5209} ..	152·5	152·7	159·4	159·8	206·2	206·8	216·4	216·9	196·5	196·3	216·4	216·9
Cd_{5086} ..	165·0	165·3	173·1	172·9	223·6	223·5	224·4	230·4	215·0	213·5	234·4	234·4
Cd_{4800} ..	203·1	203·3	211·2	211·2	275·0	276·1	285·6	285·7	260·0	260·4	285·6	285·7
Cd_{4678} ..	223·1	223·1	234·4	233·9	305·0	305·2	313·7	313·7	285·6	285·9	313·7	313·7
Li_{4603} ..	238·1	237·7	246·2	247·3	326·2	326·1	333·1	333·1	303·7	304·0	333·1	333·5
Hg_{4358} ..	299·4	299·8	309·4	309·4	415·6	415·6	415·6	415·8	378·7	378·9	415·6	415·6

Summary

(1) The rotatory dispersion of (α- and β-) naphthyl-imino- and -amino-*d*-camphors has been determined in six solvents and has been found to obey Drude's one-term equation, $[\alpha] = \frac{k_0}{\lambda^2 - \lambda_0^2}$; it is, therefore, simple.

(2) The sequence of rotatory power in the case of these compounds in different solvents is in the reverse order of the dielectric constants of the solvents except for minor variations.

(3) The β-naphthyl-derivatives have higher rotatory power than their corresponding α-isomers.

(4) The breaking of the double bond of the azethenoid group causes a phenomenal depression in the rotatory power.

(5) The racemic forms are true *dl*-compounds.

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A NEW BAND SYSTEM OF BORON MONOXIDE

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Introduction

The bunsen flame fed with boric acid gives rise to the well-known boric acid fluctuation bands. When these were photographed, it was noticed that some of them were accompanied by a number of band heads. These are particularly well marked in three of the successive fluctuation bands. They look like bands of three successive sequences somewhat like the sequences of bands in the Swan, A10, BeO, N_2-second positive, BeF and many other similar band systems. A preliminary note on these bands has been already published.[6] The present paper deals with the details of the band system observed and its possible relation to the already known band systems of BO.

Experimental Procedure, Description of Spectra and Wavelengths of Band Heads

It is observed that boric acid when put into the bunsen flame changes itself into a glassy bead. During fusion it gives out a flame which is a mixture of whitish green and reddish yellow colours. The intensity of the flame persists for a short while, but if a drop of water is put on it the glassy bead gives out the same flame again. Accordingly in the present experiments boric acid was put on an asbestos sheet held above the inner cone of the burner and water was allowed to trickle at regular intervals from a funnel held vertically above the flame. The frequency of the drops was so adjusted that the intensity of the source would remain constant. The addition of fresh quantity of boric acid on the platform was, however, necessary, but after long intervals and was done by a clean copper spoon.

The bands were also observed in the spectrum of an electric spark between two glass tubes. When a discharge of an induction coil takes place through a glass tube the latter very soon breaks into two pieces due to local heating. The two broken glass pieces themselves become the seat of the discharge and the spark starting from the brilliant yellow point discharge from one piece settles down on another point on the other glass piece. This end point is characterised by an exceptional white brilliance. The glass

tube generally cracks at several points and thus a series of smaller sparks maintained between the smaller cracks show alternately white and yellow ends. The white brilliant glow emits these diffuse fluctuation bands accompanied by the bands discussed here. It may be of interest to record that in such a spectrum no atomic lines of boron were registered. It is, therefore, concluded that the fluctuation bands are more sensitive than the lines for detection of traces of boron.

The bands were photographed on spectrographs of varying dispersion and resolving power, *viz.*, Hilger Constant deviation glass spectrograph, Fuess glass spectrograph and Steinheil three-prism glass spectrograph for the visible and Hilger F_3 quartz spectrograph and Hilger medium quartz spectrograph for the ultra-violet.

The contrast between the discrete structure and the diffuse bands is small, and the structure is comparatively more blurred in the spark spectrum than in the boric acid flame spectrum. The continuous bands in the flame spectrum appear to be relatively feeble and the discrete bands therefore stand out more distinctly over the accompanying faint continuous bands. Reproductions of some such selected plates taken for the boric acid flame are given in Fig. 1–2. Fig. 1 is an enlargement of a plate taken on the constant deviation spectrograph and Fig. 2 is a reproduction of a plate taken on the Steinheil spectrograph with medium dispersion. Higher dispersion plates could be expected to distribute the intensity of the continuous bands favourably to afford reasonable contrast to the discrete bands. This, however, does not appear to take place to any great advantage. Experience of other workers (Scheibe[9]) who have used much higher dispersion (Concave grating 3 metre radius used in the second order) is also similar. The medium dispersion that was afforded by 'Steinheil' in our case gave us, however, the possibility of measuring the discrete bands with greater accuracy than the spectrograms obtained on the Constant deviation spectrograph, though the contrast as can be seen on the negative is slightly better here.

The discrete bands accompany only three of the continuous bands. These have fairly sharp heads and are degraded towards the longer waves. Under higher dispersion and resolution some of them get resolved and appear to possess close double heads. The positions of the three groups of discrete bands in their respective continuous bands are not the same in relation to the diffuse head-like formations in the continuous group to which the discrete bands are associated. This head-like formation in each continuous band is the position of maximum blackening where the band appears to be forming a head with degradation towards the red.

It has been possible to measure five band heads in the first group. All of these bands remain single under the dispersion and resolution employed and can be distinguished without doubt from the body of the continuous band in which they lie. The second group of bands ending on the long wave-length side at 5395·2 A (18530 cm.$^{-1}$) is the longest and under the dispersion and resolution of the Constant deviation spectrograph all the bands are single headed but diffuse. In fact, some of them appear to possess two close heads under bigger dispersion and resolution excepting the two bands at 5455·9 and 5436 A. In the third group there is a large number of bands but only three of them belong to the new system. These bands also appear to be single headed. The rest are all very probably members of the already known BO systems.

Average values of wave-lengths for the discrete bands obtained in a large number of different measurements done on spectrograms obtained on Steinheil and on some of their microphotograms are listed in Table I. The comparison spectrum which afforded the standard wave-lengths was that of iron arc or (Hg + He) discharge tube spectra superposed on the main spectrum. The values obtained agreed with one another to an accuracy of 2 A. The wave numbers of the bands and their relative intensity as

TABLE I

List of discrete bands

Int.	Wave-length in air in A.U.	Wave number in vac. in cm.$^{-1}$	V′, V″	Calculated wave number in vac. in cm.$^{-1}$	O–C
2	5820·5	17176	4, 7	17178	−2
2	5802·0	17231	3, 6	17224	+7
10	5789·9	17267	2, 5	17261	+6
10	5781·0	17294	1, 4	17290	+4
7	5777·1	17314	0, 3	17309	+5
2	*5729	17450			
5	*5709·3	17510			
10	5478·5	18248	5, 7	18243	+5
5	5455·9	18324	4, 6	18317	+7
5	5435·9	18391	3, 5	18383	+8
5	5421·0	18442	2, 4	18441	+1
5	5405·9	18493	1, 3	18489	+4
7	5395·2	18530	0, 2	18528	+2
10	*5361·2	18647			
2	*5201·5	19220	0, 0 (BO Comb.)		
2	*5199·6	19227	1, 1 (BO Comb.)		
2	*5191·7	19256	2, 2 (BO Comb.)		
1	*5160·9	19371	1, 3 (BO α)		
1	5157·4	19384	5, 6	19382	+2
5	*5151·2	19408	2, 2 (BO Comb.)		
1	5131·0	19484	4, 5	19476	+8
1	5110·2	19563	3, 4	19562	+1

estimated visually on the basis of 10 for the strongest band are also given in the same table. The error in measurement is believed to be not more than ± 0·8 A or an average of 4 wave numbers in the region of the bands.

Analysis

A glance at the position of these three groups suggests a clue to their possible analysis. Normally with such a disposition of band groups which obtains in some of the well-known systems, *e.g.*, A 10, CN violet, N_2 second positive, CS, BeO, BeF to name only a few, we should naturally try to arrange bands such that the three groups form three successive sequences. Secondly, the association of these bands with the boric acid fluctuation bands suggests that the scheme arrived at would bring the bands into some relation with the already known bands of BO. With these two considerations it has been possible to arrange them in a Deslander's table. The V′V″ values thus arrived at are denoted in Table I against each band which fit into the scheme. A few bands marked (*) in the table do not find a place in the analysis. Most of these bands agree in wave-length with some of the already known bands of BO and have been denoted as such under the V′V″ column. The only bands left unaccounted for are those at 5729, 5709·3, and 5361·2 A.U. Of these the first is measured on only one plate and its presence may be doubted. The bands fall into three sequences. $\Delta v = -1$ and $\Delta v = -2$ sequences overlap the associated continuous groups and extend beyond them on the shorter wave-length side. The $\Delta v = -3$ sequence lies in the body of the corresponding group. In Table II are given the first vibrational differences for the two states involved in the new band system.

Table II

Vibrational spacings in the new system

State \ V′–V″	0–1	1–2	2–3	3–4	4–5	5–6	6–7
Upper ..	1179	1148	1122·5	1093	1066		
Lower ..			1216	1199	1173·5	1160	1142

In Table III are given the first vibrational differences for the two states involved in the known system of BO. These data are obtained from the actual observed bands in each case and refer to the distances between heads.

TABLE III

Vibrational spacings in the various known band system of BO[4]

Row No.	Molecule	System	State	0–1	1–2	2–3	3–4	4–5	5–6	6–7	7–8
1	$B^{10}O$	α	$A^2\pi$	1274	1250	1229	1204	1178	1157		
2			$X^2\Sigma^+$	1914·3	1890	1886	1841·5	1816	1798		
3	$B^{11}O$	α	$A^2\pi$	1238·2	1216·5	1196·1	1173·0	1152·0	1129·3	1113·5	1085·7
4			$X^2\Sigma^+$	1862·3	1837·5	1815·5	1791·8	1771·0	1744·5	1721·5	
5	$B^{10}O$	β	$B^2\Sigma^+$	1295·0	1272	1250·9	1230·2	1210·3	1187·4		
6			$X^2\Sigma^+$	1915·5	1889·5	1864·8	1839·7	1814·8	1788·4	1763·8	1739·6
7	$B^{11}O$	β	$B^2\Sigma^+$	1259	1237	1217	1198·6	1179·1	1160·7		
8			$X^2\Sigma^+$	1861·2	1838·3	1813·6	1790·6	1766·4	1743·4	1719·3	1695·7
9	$B^{11}O$	Combination	$B^2\Sigma^+$	1260	1239	1213					
10			$A^2\pi$	1240	1215	1195	1175	1152			
11	$B^{10}O$	Combination	$B^2\Sigma^+$	1296	1275	1254					
12			$A^2\pi$	1273	1252	1227	1205	1182			

Data on origins cannot and should not be compared with the spacings obtained here which are on band heads.

It will be seen that the term differences for the lower state are identical with those of the $B^2\Sigma$ state of $B^{11}O$ molecule tabulated in rows 7 and 9 of Table III. This proves the correctness of the V″ numbering and shows that the new bands are due to $B^{11}O$ and involve the already known $B^2\Sigma$ as their final level.

It is to be noted that all the three sequences are negative sequences on the long wave-length side of the $\Delta v = 0$ sequence which is definitely not present. The $\Delta v = -1$ sequence is also weak. It is only $\Delta v = -2$ sequence and the $\Delta v = -3$ sequence which are fairly well developed. The intensity distribution is thus rather peculiar but is analogous to one met with in a number of instances. Thus the comet tail bands due to CO^+ comprise only sequences in which Δv has a positive value. In the combination bands of CO^+ there is no band with V = 0, 1 or 2, all the bands comprising $\Delta v = 0$ or a negative value. Similarly the NO_β system comprises mostly bands for which Δv is negative.

The term differences of the new system, as can be seen from Tables II and III agree better with the term differences of the initial of the β system for $B^{11}O$ molecule than with those of the $B^{10}O$ molecule and one could expect to find a parallel system of bands due to $B^{10}O$ molecule. But a reference to

literature indicates that the $B^{10}O$ bands are weak and fragmentary and it is likely that none of them is observed here where even the $B^{11}O$ bands are not very strong. At first it was thought that the close doublet components of the bands in the second group might be due to the isotopic molecules, but calculation shows that the differences observed are not of the order expected. It is also difficult to explain on this basis the fact that the two or three of the bands of this group are not double but single. This also excludes the possibility of the doublet head being due to a Q branch. It is not possible to explain the existence of this doublet structure in only a few heads with any certainty but it is likely that they may be the subsidiary heads arising out of certain branches which show these heads only under conditions which might be favourable just for these bands. As an example of such a circumstance we may mention the visible oxygen bands due to O_2^+.

We now proceed to obtain an equation to represent the bands. The term differences for the lower state, as we have seen, agree very well indeed with the corresponding ones for $B^{11}O$, $B^2\Sigma$ state. The vibrational function for this state can, therefore, be adopted for the final state of the new bands. Before doing so, however, a simple formula was developed assuming the second differences to be constant and given by the average value in each case. This yields the following equation:—

$$\nu_{head} = 21030 + (1193{\cdot}3\ V' - 14{\cdot}3\ V'^2) - (1268{\cdot}7\ V'' - 9{\cdot}7\ V''^2).$$

The final vibrational function may now be compared with the one known from the data on bands involving this level. The data on BO bands available in all reference books on molecular spectroscopy (3, 10, 11) refer, however, with origins of bands. According to the data of Mulliken[4,5] which refer to the heads, the vibrational function for the $B^2\Sigma$ state is

$$1268{\cdot}8\ V - 9{\cdot}98\ V^2.$$

We, therefore, adopt this value and rewrite the above equation for the new bands as follows :—

$$\nu_{head} = 21030 + (1193{\cdot}3\ V' - 14{\cdot}3\ V'^2) - (1268{\cdot}8\ V'' - 9{\cdot}98\ V''^2).$$

The wave-numbers calculated according to this equation for the various bands are given in Table I and the corresponding (O−C) values are denoted in the last column of the same table. It will be seen that the agreement is very satisfactory in view of the possible error in the measurements of the band heads and of the fact that the equation developed is not for the origins but for the heads.

The analysis shows that the bands are very probably due to $B^{11}O$ molecule and arise in a transition from a hitherto undiscovered electronic

level which we shall call the C level to an already known level, namely the $B^2\Sigma$ level of the $B^{11}O$ molecule at $\nu = 42865{\cdot}2\ cm.^{-1}$ The origin of the new band system being at $21030\ cm.^{-1}$, this new electronic level lies at

$$= 42865{\cdot}2 + 21030$$
$$= 63895{\cdot}2\ cm^{-1}.$$
$$= 7{\cdot}9\ e.v.,$$

above the level $X\ ^2\Sigma^+$. From the similarity of the vibrational differences in the final state it is concluded that all these bands are due to the more abundant isotope molecule $B^{11}O$. Bands belonging to the other isotope molecule $B^{11}O$ do not seem to be present. But this remark is to be taken with reservation because the band system lies interspersed with the so-called boric acid fluctuation bands, so that against the continuous background it is possible that $B^{11}O$ bands which will be very weak may have been masked. This is further plausible when we consider the fact that even in the other three known systems of the BO molecule bands due to $B^{10}O$ isotope molecule are very fragmentary and weak indeed.

The new level is designated as C level, but it is possible to arrive at a more definite description of this electronic level. The fact that for each vibrational transition there is only one band head, (except for some of the bands in group second which show a double head and which is very probably a subsidiary head) indicates the absence of Q branches and therefore of Q heads. This means that the new level has got the same Λ value as the $B^2\Sigma^+$ level or in other words that it is also a Σ level. As regards its multiplicity it is not possible to be quite definite.

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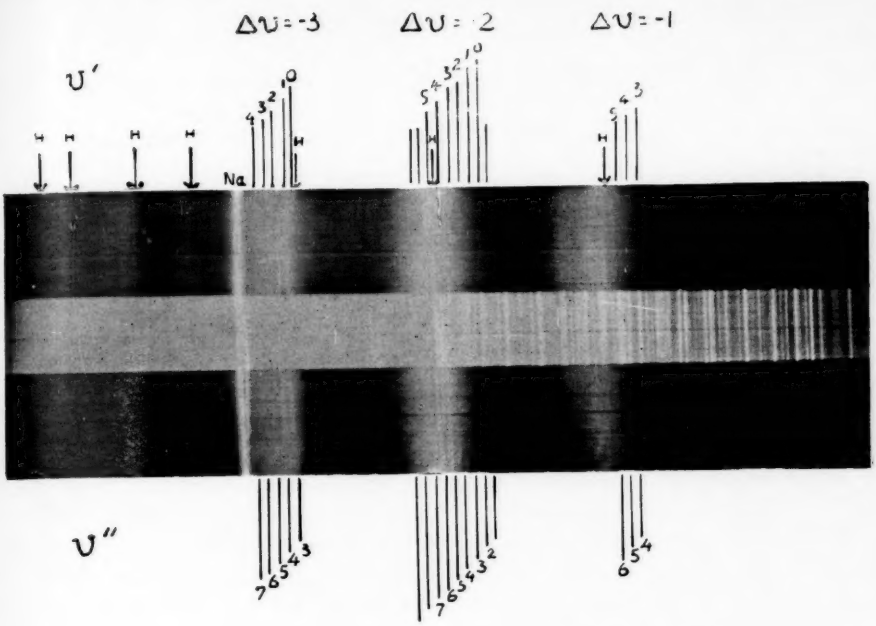

FIG. 1 An enlargement of the spectrum of boric acid flame.
H = Head-like formation in a diffuse band

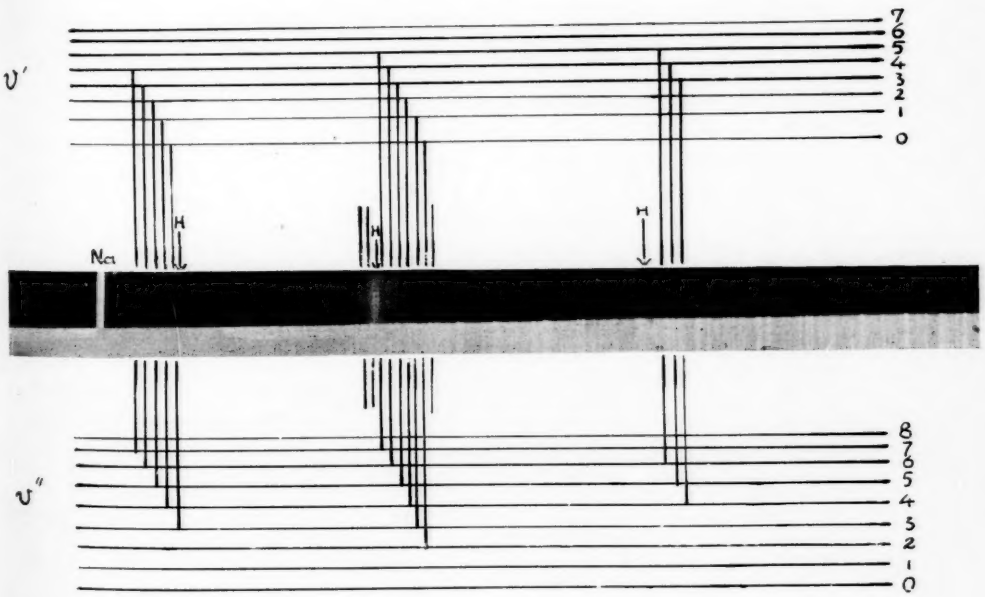

FIG. 2. Spectrum of boric acid on Steinheil.
The continuum is suppressed.

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DECCAN TRAP OUTLIERS OF THE GODAVARI DISTRICTS

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The outliers of Deccan traps north of Rajahmundry, in East Godavari District, and near Pangudi, in West Godavari District, have attracted the attention of Geologists for over a century now on account of their separation from the known limits of the present margin of the main Deccan trap formation by about 200 miles. The earliest reference to this area is by Benza and Cullen (1837) who published a report on the Deccan traps and associated Inter-trappeans of Rajahmundry area. Subsequently, Elliot and Hislop (1850–1860), and King (1880) described the outlier as one of the most interesting formations and an important clue to the correlation of the volcanic rocks with the known series of fossiliferous rocks. Later Das Gupta (1933) visited the area and collected from the Infra-trappean sandstones south of Duddukur a species of Cardita which he identified as *C. beaumonti*. Discussing the age of the above fossil *Cardita beaumonti* he assigned to the Infra-trappean sandstones an upper cretaceous period. Subsequently Rao and Rao (1935, 1937, 1939) recorded the occurrence of numerous fossil Charophyta and Formanifera in the Inter-trappean beds of this region. From a study of these fossils, they regarded that the Deccan trap flows of this region are of an early Tertiary age. The most recent contribution is by Krishnan (1941) who summarises his geological observations while emphasizing the economic aspects of the area. As analytical data of the rock types in conjunction with field studies are of particular interest for purposes of correlation, this paper records the results of such a work.

Geology of the area.—The area is defined by 17° to 17° 5′ (Lat.) and 81° 30′ to 81° 51′ (Long.), and includes the region from east and north-east of Rajahmundry to west of Devarapalli in the Godavari districts and is about 150 sq. miles.

The Deccan trap outliers with the associated Inter-trappeans gently rise from the alluvial plains on either side of the Godavari river and attain a height of about 250 ft. above general level. The outlier north-west of

Rajahmundry underlies the Rajahmundry sandstones believed to be of Tertiary age, while near Pangudi it forms two flat-topped hills succeeding with a distinct unconformity the Infra-trappean sandstones at Duddukur. Hard and compact trap makes its appearance at Duddukur and extends upto Gouripatnam towards north, and Lakshmipuram towards south. Beyond Pangudi, the trap disappears under the Godavari alluvium and at a distance of twelve miles from the above village, it crops out again on the east bank of the river near Kateru, situated two miles north-west of Rajahmundry.

The greatest thickness of the traps, as observed at Pangudi, is about 200 ft. In the Rajahmundry area, south of the T. B. Sanatorium, about two hundred yards east of Kateru, the upper trap is more than 70 ft. in thickness while that of the lower flow cannot be estimated as it is not exposed fully. The existence of two flows in this region is apparent; Krishnan (1941) divides the top formation into two flows. Lithologically the trap is a fine to medium-grained, hard and compact rock with a subconchoidal to conchoidal fracture. Amygdaloidal cavities with quartz, cryptocrystalline silica, agate, chalcedony, opal and zeolites are fairly abundant. Ramifications of thin veins of quartz measuring upto a centimetre in thickness run in all directions especially in the lower horizons of the traps. The amygdales and geodes occur more commonly in the Pangudi region where the exposures cover a large area, the surrounding fields being strewn with agate, chalcodony and quartz fragments released by the disintegration of the traps. The whole surface of the trap rock shows numerous pitch-dark patches, one to three millimetres in size representing presumably the alteration products of interstitial glassy material.

The traps are nearly horizontal and occasionally show an inclination upto 4° due to local slumping.

Mineralogy of the rock-types.—The Godavari traps are typically basaltic with an average specific gravity of 2·99 and can be divided into two types on the grain size as follows:

1. Fine-grained basalt of Pangudi area.
2. Medium-grained basalt of Kateru region.

In the former type the grain size averages from 0·2 mm. to 0·5 mm. while in the latter type from 0·5 mm. to 1 mm. The chief constituent minerals are the plagioclase felspars, pyroxenes and opaque ores with subordinate amounts of altered glass. The following paragraphs record the description of the various constituents of the traps in the order of relative abundance.

Felspar.—The felspar represented by a medium to basic labradorite occupies about 40 to 50 per cent. of the bulk volume of the rock and occurs as laths twinned as on albite law. The laths vary in their size from 0·2 mm. in the fine-grained basalts from Pangudi to 1 mm. in the medium-grained basalts from Kateru. Though they appear sometimes as isolated idiomorphic prisms they occur mostly as glomero-porphyritic groups. Determinations by the universal stage method reveal the presence of complex twins such as albite-menabach, menabach-ala and albite-ala besides simple twins. Measurements on the twinning lamellæ give extinctions upto 37° corresponding to a labradorite of composition about Ab 30 An 70. From the optic axial angles and the twinning laws the anorthite content, as deduced with the help of Federov-Nikitn graphs, as described by Reinhard (1931), ranges from 55 per cent. to as much as 65 per cent. The anorthite content determined from optic axial angle and twin laws shows discrepancy. This may be due to the presence of orthoclase in plagioclase in solid solution. Krishnan (1926) and Barth (1936) report such discrepancies in the determination of the anorthite content of plagioclase felspars in basalts. They contend that the content of potash in basaltic felspars is not always negligible and that basaltic felspars do not generally belong to the pure plagioclase series but contain a certain proportion of orthoclase in plagioclase. Table I shows the presence of 5 to 6 per cent. of normative orthoclase in plagioclase felspar in solid solution in all the plateau basalts including the traps in this region.

The Plagioclase laths are fresh looking though often surrounded by brownish or greenish palagonite.

Pyroxene.—The next abundant and important constituent is the pyroxene, colourless in thin sections. The pyroxene is optically positive with the optic axial angle ranging from 15°–42° and with the optic plane parallel to (010). Most of the pyroxenes show low optic axial angles below 32° while a few grains show a higher optic angle above 32°. In a recent paper, Hess (1941) groups all pyroxenes with optic angle below 32° under pigeonite, while pyroxenes above 32° under augite. Since pyroxene grains show both low and high optic angles it is inferred that both of them exist as two separate phases in the Deccan traps of this region.

Table II gives a comparative study of the meta-silicates $CaSiO_3$, $MgSiO_3$ and $FeSiO_3$ of the pyroxenes of a few selected basalts. Though a reciprocal relationship exists between $MgSiO_3$ and $FeSiO_3$, the meta-silicates of the rocks under study are more or less uniform with a low content of $CaSiO_3$. Moreover, the average meta-silicate composition of these rocks does not

TABLE I

Composition of the Plagioclase felspar

Sample	Total normative felspar in % of the whole rock	Composition of the felspar		
		Orthoclase	Albite	Anorthite
A ..	47·3	6	46	42
B ..	49·1	6	48	44
C ..	44·4	6	38	44
D ..	41·0	6	36	40
1 ..	38·6	6	46	48
2 ..	51·1	7	49	44
3 ..	41·1	4	43	53
4 ..	44·2	5	62	33

A. Pangudi Trap, Analyst : E. Venkayya.
B. Duddukur Trap, Analyst : E. Venkayya.
C. Kateru South, Analyst : E. Venkayya.
D. Kateru Main quarries, Analyst : E. Venkayya.
1. Hawaiian Basalts, *Amer. Jour, Sci.*, 21, pp. 518–520, 1931.
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TABLE II

The normative composition of the pyroxenes in the Godavari traps and other basalts

Samples	Diopside	Hypersthene	$CaSiO_3$	$MgSiO_3$	$FeSiO_3$
A ..	20·81	14·20	30·02	37·40	32·58
B ..	18·95	14·04	29·2	38·8	31·9
C ..	14·96	20·68	21·5	47·5	31·0
D ..	20·75	16·43	28·4	40·4	31·2
E ..	18·87	16·34	27·30	42·00	30·7
1 ..	17·41	17·78	24·6	44·3	31·3
2 ..	14·71	21·08	20·3	53·9	25·3
3 ..	13·14	15·90	22·30	52·3	25·4
4 ..	16·76	25·74	19·6	46·6	33·8

A to D. Godavari Traps, Analyst : E. Venkayya.
E. Average of the above four analyses.
1. Average of 11 analyses of Deccan traps, H. S. Washington, *Bull. Geol. Soc. Amer.*, Vol. 33, pp. 765–804, 1922.
2. Average of New Jersey Basalt. Anderson, *Amer. Jour. Sci.*, 7, pp. 477–92, 1928.
3. Average of six analyses of Whin Sill and the related dykes of North of England, *Min. Mag.*, 21, pp. 493–542, 1928.
4. Average of Karroo dolerites, Daly, R. A. and Barth, T. F. W., *Geol. Mag.*, 67, pp. 97–110, 1930.

differ much from that of Washington's analysis, while the New Jersey basalt, Whin Sill and related dykes, and the Karroo dolerites show a higher percentage of $MgSiO_3$ and lower amounts of $FeSiO_3$ as is the case with all the plateau type of basalts. The metasilicates when plotted after the method of Hess (1941) fall, however, in the pigeonitic field. This may point to the fact that most of the pyroxenes are pigeonitic in their optical characters.

The relative order of crystallisation of pyroxenes and felspars has been determined with the help of the formula (Barth, 1936).

$$ab' + 2di' + 2{\cdot}3hy' = 123.$$

The normative constituents albite, anorthite, diopside and hypersthene are recalculated to 100 and using the above formula, the (f) norm is determined. Should the sum equal to 123, the basalt lies on the boundary surface of a tetrahedron, the four corners of which represent the four above constituents when simultaneous crystallisation ensues in the magma. On the other hand if the sum totals to below 123 or above 123, the basalt lies in the plagioclase field or pyroxene field separating either plagioclase or pyroxene respectively during the process of crystallisation. Table III records the (f) norm of the traps under study and other plateau basalts in which either plagioclase or pyroxene is the earlier mineral to crystallise.

TABLE III

The relative order of crystallisation of felspars and pyroxenes in basalts

Samnles	Albite ab′	Anorthite an′	Diopside di′	Hypersthene hy′	Total (f) norm
A ..	23·58	21·41	20·81	14·20	122·0
B ..	24·63	21·13	18·95	14·04	120·0
C ..	18·39	20·85	20·75	16·43	127·0
D ..	19·39	22·24	14·96	20·68	123
E ..	21·5	21·4	18·8	16·3	123·00
1 ..	27·0	29·0	22·0	22·0	122·0
2 ..	31·5	26·5	15·5	26·5	123·5
3 ..	20·5	22·5	20·5	26·5	122·5
4	26·5	29·5	20·0	24·0	122·0

A to D. Godavari traps, Analyst : E. Venkayya.

E. Mean of the four analyses.

1. Deccan traps. Average of 11 analyses, H. S. Washington, *Bull. Geol. Soc. Amer.*, **33**, pp. 765–804, 1922.
2. Oregon traps. *Ibid.*, 1922.
3. Karroo dolerites. R. A. Daly and T. F. W. Barth, *Geol. Mag.*, **67**, pp. 97–110, 1930.
4. All plateau basalts, (Average of 43 analyses), R. A. Daly, Igneous rocks and the depths of the earth, New York, pp. 17, 1933.

In all the specimens the total of the felspars and pyroxenes is very nearly equal to 123, thus showing simultaneous crystallisation. However, it seems from the idiomorphic nature of the two minerals that plagioclase separated out first, immediately followed by pyroxene, and later both have crystallised simultaneously. It is interesting to note that the average (f) norm for the Godavari traps coincides with the mean of the plateau basalts and in particular with that of Deccan traps.

The pyroxenes are colourless without any distinct pleochroism but often tinged with a slight violet colour probably due to the presence of traces

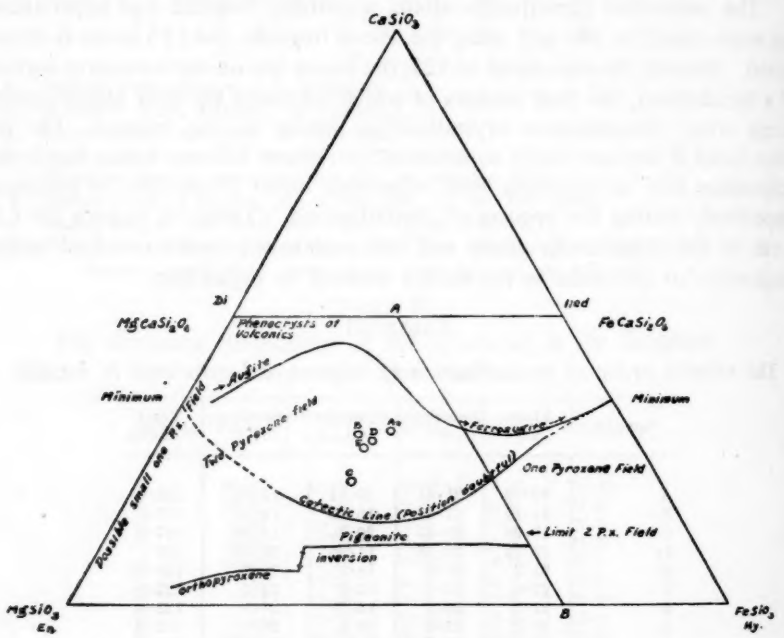

FIG. 1. Fields of Pyroxenes (After H. H. Hess).

of titanium. Both in fine and course-grained varieties they are sub-idiomorphic or granular with well-developed cleavages. Under ordinary light, they appear to enclose prisms of felspars. But on crossing the nicols, the Pyroxenes seem to be aggregates of numerous granules with random orientations rather than single prisms. Instances are recorded where small felspar laths project into relatively large pyroxene prisms giving rise to a sub-ophitic texture.

The chief alteration product of the pyroxene is brown or green palagonite. If alteration takes place in association with magnetite, the resulting substance is brown palagonite, while the green variety develops due to the alteration of the pyroxenes in association with glass.

Opaque ore-minerals.—The Deccan traps contain a higher percentage of iron than most other plateau basalts. In rocks rich in brown palagonite or dark brown glass, the minerals are either obscured or appear in the form of fine dust suggesting that it tends to be concentrated in the glassy portion. In the fine-grained traps from Pangudi it forms roughly equidimensional granules occupying interspaces between the felspar crystals while in the medium-grained variety from Kateru it occurs both as granular and also as skeletal crystals or bars. This is of especial interest as it connotes the late stage crystallisation of iron in basaltic magmas. Washington (1922) and Krishnan (1926) similarly record the late stage crystallisation of opaque ores in Deccan traps.

Primary Glass.—The primary glass, when fresh, is of light brown colour and shows incipient crystallisation with minute grains of iron all over its surface. Often this shows devitrification, to a fibrous substance of low refractive index.

Besides the above primary constituents the trap rocks are known for their number and variety of secondary constituents derived mostly by the alteration of the primary minerals. The chief alteration products being palagonite, chlorophæite, celadonite and delessite (Fermor, 1926). Of all these, only two secondary minerals, palagonite and chlorophæte, have been identified in these rocks.

In the Kateru basalts, palagonite occurs as spherules or irregular patches varying from 1 mm. to 3 mm. in width with pitch dark colour and no regular orientation. Under the microscope, each spherule or patch shows a dark brown colour with very characteristic concentric undulating bands or zones of growth in some cases exhibiting parallelism to one another. The refractive index rises both with the passage from the glassy to devitrified condition and also with increasing intensity of the colour. The brown palagonite in a few instances is seen passing into another altered variety identified as chlorophæite.

Petrology of the rock types.—A brief megascopic and microscopic description of the rock types met with in the area is given in the following paragraphs.

A. *Fine-grained basalt from Pangudi.*—200 yds. east of Lingakonda. The rock is dark grey and fine-grained with conchoidal fracture.

Under the microscope the rock is composed mainly of labradorite laths, Pyroxene in ophitic to sub-ophitic relationship to the felspars, opaque ore minerals, and subordinate amounts of glass which has altered in some places to green chlorophæite. The anorthite content of labradorite approximates to about 65 per cent.

B. *Fine-grained basalt from Duddukur.*—On the top of Duddukur metta from a depth of about 15 feet from the surface. In hand specimen the rock is very similar to the above specimen (A).

C. *Medium-grained basalt from Kateru.*—Collected from a depth of about 10′ from the surface in the open quarries about six furlongs south-east of Kateru. The rock appears dark greyish green in colour with black spots all over the surface. It differs from the above two specimens in being medium grained.

The rock shows relatively large felspar laths and pyroxene grains, the latter often partly enclosing the felspar laths giving rise to sub-ophitic texture. Dark brown palagonite forms at the expense of augite and opaque ores.

D. *Medium-grained basalt from Kateru.*—The specimen was collected in the Kateru quarries at a depth of about 60 feet from the surface. The rock is dark green in colour and shows dark patches all over the surface.

Under the microscope, the rock appears decidedly coarser grained than the previous one with the plagioclase measuring upto one millimetre enclosing tiny plagioclase laths in a sub-ophitic fashion. The ground mass consists of abundant dark brown glass interstitial to the pyroxenes and plagioclases.

Discussion

The above described four types were analysed and Table IV shows the weight percentages, the C.I.P.W. norm and Niggli values of the main constituents. Besides the above data three more analyses of the Deccan traps of the Central Provinces were also given for a comparative study. The similarity in the chemical composition and the norms between the Deccan traps of the two regions is clear though a distance of more than 200 miles intervenes between the margins of the two flows. The analyses show orthoclase ranging from 2·78 per cent. to as much as 3·88 per cent. in solid solution in plagioclase. Occult quartz, though subordinate in amount, varies from 2·46 to 6·54 per cent. It can be inferred that at the low silica end of the series, the rocks grade into ultra-basic types, while with the increase of silica olivine is resorbed, and reacts with the melt giving rise to pyroxene. The nature and composition of the pyroxene that crystallises later depends upon

TABLE IV

Comparative study of the Godavari and Central Provinces Traps

Weight per cent.	A	B	C	D	E	F	G
SiO_2 ..	49·98	49·92	49·78	49·71	49·06	49·78	49·28
Al_2O_3 ..	13·15	13·21	12·41	11·72	11·66	11·80	11·69
Fe_2O_3 ..	4·21	4·42	4·57	4·68	3·26	2·83	3·04
FeO ..	10·62	10·21	10·80	11·23	11·53	11·86	11·79
MgO ..	5·23	5·12	6·78	6·01	5·01	5·13	4·96
CaO ..	9·42	8·97	8·29	9·37	10·44	10·36	10·49
Na_2O ..	2·82	2·94	2·32	2·23	2·27	2·75	2·51
K_2O ..	·61	·67	·59	·52	·70	·63	·68
TiO_2 ..	2·81	2·73	3·00	3·01	3·20	3·20	3·23
H_2O ..	1·23	1·65	1·53	1·70	2·90	1·60	2·53
C. I. P. W. Norm—							
Qz ..	3·9	4·26	5·88	6·54	5·40	2·46	3·60
Ortho ..	3·34	3·34	2·78	2·78	3·89	3·89	3·89
Alb. ..	23·58	24·63	19·39	18·34	19·39	23·06	20·96
Anor. ..	21·41	21·13	22·24	20·85	19·48	18·07	18·90
Diop. ..	20·81	18·95	14·96	20·75	24·18	26·54	26·28
Hy. ..	14·20	10·04	20·68	16·43	13·70	14·12	13·20
Mt. ..	6·03	6·50	6·50	6·73	4·64	4·18	4·41
Il. ..	5·32	5·17	5·78	5·93	6·08	6·08	6·08
H_2O ..	1·23	1·65	1·58	1·70	2·90	1·70	2·41
Niggli values—							
si ..	123·0	118·7	114·6	117·0	121·89	121·4	121·63
al ..	17·9	18·5	17·0	16·7	17·07	16·96	17·00
fm ..	46·3	46·5	51·8	48·6	48·58	48·50	48·18
c ..	23·6	22·7	20·0	23·5	27·78	27·05	27·74
alk ..	7·1	7·5	5·8	5·9	6·57	7·49	7·07
ti	5·0	4·8	5·2	5·5	5·98	5·84	5·99

A to D. Deccan traps, Godavari districts, Analyst : E. Venkayya.

E. *Rec. Geo. Surv. India.* Vol. LXVIII, Pt. 3, pp. 33, 1934, Flow (1). Analyst : M. Raoult.

F. *Ibid.*, pp. 350, Analyst : M. Raoult.

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the relative amounts of CaO, MgO, and FeO, and the rate of cooling and crystallisation. An excess of CaO results in the development of diopside and a relatively low content of CaO with a concomitant concentration of MgO and FeO results in the separation of pyroxene with low content of CaO.

As is evident from the optical data, that in the Deccan traps in general, much of CaO must have been taken up by the early formed plagioclase laths to build up idiomorphic prisms thus impoverishing the magma in CaO. During the period of crystallisation, any olivine that has separated may be in the process of resorption and reaction with the surrounding magma to give rise to pyroxene at a latter stage. Hence by the time pyroxene begins to crystallise the magma has been depleted of its CaO content due to the development of basic plagioclase felspars with a concomitant enrichment in MgO and FeO molecules, and subsequently developed sub-hedral and

anhedral granules of pyroxene interstitial to felspars. Further, the nature of the pyroxene depends on the relative proportions of MgO and FeO available during the period of crystallisation. If the ratio of the two oxides MgO: FeO, reaches 7: 3 or less than this (*i.e.*, any increase in the proportion of iron relative to MgO) a pigeonitic pyroxene separates out from the magma depending on the rate of cooling. This crystallisation of pigeonite is further facilitated by the rapid cooling of the magma during the period of consolidation, as pigeonite according to Tsuboi (1932) constitutes a solid solution of En, Hy, Di, Hed. An interesting fact that emerges from this study is that in all plateau type of basalts occupying enormous areas in various parts of the globe, due to rapid crystallisation of the magma the ratio between MgO and FeO seems to be always less than 7 : 3 thus favouring the crystallisation of a pigeonitic pyroxene. In his studies on the crystallisation process of basalt, Barth (1936) states that the pyroxene in the basaltic rocks of the Pacific, South Africa, India and Cape Verde Islands are all pigeonitic in character. Tsuboi (1932), concurring with the views expressed by Barth, points out that the pyroxenic end members En–Hy–Di–Hed. are only partially miscible in the plutonic stage while they show complete miscibility in the effusive stage. Hence the small grain size and the pigeonitic character of the pyroxene suggests that the lavas should have been poured out simultaneously with the crystallisation of pyroxenes in the magma. Any excess of iron either crystallised as such at a latter stage or combined with titanium giving rise to ilmanite plates and bars.

Analyses of the four rock types show low percentages of silica, alumina and alkalies relatively to magnesia, iron and calcium. This points to the fact that the Deccan traps have not disclosed any degree of differentiation. Owing to the undifferentiated nature, it is not possible to construct variation diagrams from Niggli values since ' Si ' ranges from 114 to 123 with a difference of 9 only. However, it is interesting to find a close similarity in chemical composition between the Deccan traps of this region and those of Central Provinces though the margins of the two outliers have been separated by a distance of more than 200 miles. This lends support to the view that these basic rocks of the Rajahmundry area are genetically connected to the main Deccan trap extrusion.

In a recent paper Vemban (1947) critically reviews the available analytical data on the Deccan Traps and comes to the conclusion that there does not seem to be much evidence for the existence of two separate basic magmas and that a single magma type more basic than plateau basalts would appear to be adequate to account for the evolution of the rocks in the Deccan trap assemblage.

Summary

The Deccan trap outliers of the Godavari districts were studied both in the field and laboratory. Microscopic investigations reveal that the traps are basaltic in their characters showing labradorite, pyroxene, interstitial glass and subordinate amounts of opaque ore-minerals. Four rock types were analysed and the analyses show low percentages of silica, alumina, and alkalies relatively to magnesia, iron and calcium. It is interesting to find a close similarity in chemical composition between the Deccan traps of this region and those of Central Provinces, though they have been separated by a distance of more than 200 miles. This lends to support to the view that the traps of the Rajahmundry are genetically connected with the main Deccan trap outliers.

The author expresses his grateful thanks to Prof. C. Mahadevan for suggesting the problem and guiding him throughout the course of the work.

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THE EFFECT OF ELECTRIC FIELD ON THE DEGREE OF DEPOLARISATION OF LIGHT SCATTERING IN COLLOIDAL SOLUTIONS

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Krishnan[1] has investigated the variation of the depolarisation factor in graphite sols by orienting the colloidal graphite particles by means of the magnetic field. Hoover[2] on the other hand, has tried the influence of electric field on the monodispersed bentonite sols but he could not notice any change in the depolarisation factor on application of the electric field. Subramanya and others[3] investigated the effect of electric field on the intensity of the Tyndall scattering by passing a beam of polarised light through graphite, stearic acid and benzopurpurine sols. They noticed that the intensity of the scattering would depend upon the direction of the electric field and also on the nature of the sol employed, but quantitative data on the depolarisation factor was not obtained.

In the present paper the effect of electric field on the degree of depolarisation of Tyndall scattering has been investigated in detail using the following aqueous sols: (1) graphite, (2) stearic acid, (3) vanadium pentoxide, (4) benzopurpurine. The first two sols contain disc-shaped colloidal particles, while the third and the fourth contain rod-shaped particles. The depolarisation factors ρ_u, ρ_v and ρ_h have been studied using the electric field (1) perpendicular to the incident beam and the direction of observation, (2) perpendicular to the incident beam but parallel to the direction of observation and (3) parallel to the incident beam but perpendicular to the direction of observation.

Experimental

1. *Preparation of the Sols*

Graphite sols.—The graphite sol was prepared by the method of Krishnan[4] by shaking up 2 g. of aquadag with 200 c.c. of water on a shaking machine for one hour. The resulting mixture was centrifuged for one hour and the supernatant liquid was again filtered through a Whatman No. 31 filter-paper to remove the suspended solids. The sol prepared in this manner

was very dark and was suitably diluted before use. The average diameter of the graphite particles as determined by the slit ultra microscope was 138 m. μ.

Stearic acid.—A solution (10%) of stearic acid (A.R.) in methyl alcohol was poured into boiling water (200 c.c.) drop by drop till a thick emulsion was obtained. The emulsion was boiled for 5–6 hours to drive off the alcohol completely. It was then cooled and filtered. This solution was also suitably diluted before use. The percentage of stearic acid in the sol was 0·012 and the average diameter of the particles was 236 m. μ.

Vanadium pentoxide.—About 3 grams of pure ammonium vanadate were ground well with about 20 c.c. of 10% hydrochloric acid. The resulting precipitate was washed well on a filter-paper till the filtrate was coloured orange red. The precipitate was then shaken up with 200 c.c. of water for 5–6 hours on a shaking machine and dialised in the cold for 48 hours. After dialysis the colloidal solution gave no test for the chloride. The sol was then filtered through No. 31 filter-paper and suitably diluted before use. The vanadium pentoxide content was 0·022%. In this case the particle size as determined by the ultra-microscope is not accurate on account of the solubility of vanadium pentoxide.

Benzo-purpurine sol.—The C.P. benzopurpurine was specially purified by the sodium acetate method described by Robinson.[5] The solid obtained was 98% pure as indicated by the ignition test. The sol was prepared by dissolving the solid in a suitable quantity of water. The percentage of benzopurpurine in the sol employed was 0·018. Even in this case the particle size could not be determined on account of the solubility of benzopurpurine in water.

2. *The Optical Arrangement*

The optical arrangement that was used to determine the depolarisation factor was similar to the one used by Mata Prasad and Guruswamy.[6] The light from a point-o-lite lamp (500 c.p.) was condensed on a glass cell containing the colloidal solution by means of a lens of long focal length (50 cm.). The glass cell had optically plane surfaces and was surrounded by a water-bath to maintain the temperature of the sol constant. The effect of secondary scattering was considerably reduced by having a thin incident beam (3 mm. × 2 mm.) and also by measuring the intensity of the scattered light within one centimetre after the passage of the incident beam through the liquid. The glass cell was covered with a dark paper having 3 holes, two for the entrance and exit of the incident beam and the third for viewing

the scattered light. As usual the depolarisation factor of the scattered light was determined by the Cornu's method.

3. *Application of the Electric Field*

Two platinum electrodes of a conductivity cell (1 cm. × 2 cm.) arranged one above the other were employed to apply the electric field perpendicular to the incident beam and also to the direction of observation. The potential gradient was altered by including an external resistance in the circuit. The electrodes were given a coating of platinum black to prevent the reflection of light.

In applying the field parallel to the incident beam and perpendicular to the direction of observation, two vertical platinum electrodes (1 cm. × 2 cm.) were placed parallel to one another at a distance of 1 cm. Each electrode had a hole (3 mm. × 2 mm.) at its centre for the inlet and the exit of the incident beam. In the next case where the field had to be perpendicular to the incident beam but parallel to the direction of observation, the two platinum electrodes having the apertures were turned at right angles so that the scattered light passed through the apertures of the electrodes while the incident beam passed between them. To avoid polarisation, alternating current (60 cycles) was employed to produce the electric field.

4. *Measurement of the Degree of Depolarisation*

Graphite sols.—The graphite sol was perhaps the best system used to investigate the depolarisation factor as the secondary scattering was practically eliminated on account of the high absorption by the colloidal particles. The image of the light scattered was very sharp and the values of the depolarisation were very accurate. Three to four independent readings were taken for the measurement of θ and the different values did not differ from the mean by more than 0·3°. On the application of the field, there were distinct changes in the intensity of the light scattered and the change in θ could easily be noted. Since the electrolyte content of the solution was very small, there was practically no heating effect on the application of the electric field.

During the measurement of ρ_u with the electric field perpendicular to the incident beam and also the direction of the observation, it was noticed that when the field was applied, both the vertical and horizontal components of the scattered light would increase in intensity; but the horizontal component was brighter than the vertical component. Similar observations were made during the measurement of ρ_h also. But during the measurement of

ρ_v the vertical component increased in intensity more than the horizontal component on the application of the field. For the remaining two positions of the electric field there was general darkening on the application of field and consequently the different values of θ would often differ from the mean by 0·5–0·7°. On account of the darkening, voltages higher than 180 could not be employed to determine the changes in the depolarisation factor.

Subramanya and others[3] pointed out that the depolarisation factor was a function of the concentration and in general attained a constant value at higher dilutions. But the intensity of the scattering was too low in highly diluted solutions which made the depolarisation values very inaccurate. Hence only two solutions of suitable concentrations were employed during the present investigation.

Stearic acid sols.—In the case of stearic acid sols, the secondary scattering was large and the image of the scattered light was not so sharp as in the case of graphite sols. But when the electric field was applied the image of the scattered light became quite sharp and the accuracy of the values increased. When the scattered light was viewed through the double image prism, a slight colour difference was noticed between the two images of the scattered beam. Subramanya[3] also met with similar difficulties in the case of stearic acid, but by using coloured filters, he was able to overcome these difficulties. But in the present work use of filters had to be avoided in order to maintain the uniformity of the illumination with the sols investigated. As in the case of graphite sols there was very little heating effect when the electric field was applied. Three concentrations of stearic acid sol were employed for the present investigation.

Vanadium pentoxide sols.—While using these sols, high concentrations of the vanadium pentoxide had to be avoided since there was too much of heating effect on the application of the electric field. Unlike the previous case, no difficulty was experienced in matching the images of the scattered beam through the double image prism. The values of θ did not often vary from the mean by more than 0·5°.

Benzopurpurine sols.—This case was similar to that of vanadium pentoxide sols. High concentrations of the sol had to be avoided on account of the heating effect of the electric field. The images got were a bit less sharp than in the case of vanadium pentoxide. Two concentrations of the sols were used in this case.

The details of the results are given in the following Tables:

TABLE I A

Graphite sol: *Average diameter of the particle* = 138 *m.* μ.
Field: *Perpendicular to the incident beam and also to the direction of observation.* (*Position A*)

V = vertical component; H = horizontal component of the scattered light when field is applied

	Conc. of the sol = 0·0008%					Conc. of the sol = 0·0004%			
	V	Brighter	Bright	Bright		Same as in the previous concentration			
	H	Bright	Brighter	Brighter					
Field		ρ_v	ρ_h	ρ_u(obs.)	ρ_u (cal.)	ρ_v	ρ_h	ρ_u(obs.)	ρ_u(cal.)
Volt/cm.									
0	..	6·8	26·0	35·5	33·1	7·0	23·6	33·1	34·4
60	..	4·8	13·3	41·5	39·4	4·6	14·4	34·2	34·8
120	..	4·3	10·6	42·5	43·1	3·9	11·5	34·5	36·7
180	..	3·5	7·8	45·2	46·8	3·6	10·4	36·4	36·5
360	..	3·6	7·2	48·5	51·5	3·2	10·3	36·8	36·6

TABLE I B

Graphite sol: *Field*: *Perpendicular to the incident beam but parallel to the direction of observation.* (*Position B*)

	Conc. of the sol = 0·0008%					Conc. of the sol = 0·0004%			
	V	Dark	Dark	Dark		Same as in the previous case			
	H	No change	Darker	Darker					
Field		ρ_v	ρ_h	ρ_u(obs.)	ρ_u(cal.)	ρ_v	ρ_h	ρ_u(obs.)	ρ_u(cal.)
Volt/cm.									
0	..	6·8	26·0	35·5	33·1	7·0	23·6	33·1	34·4
60	..	10·2	35·0	28·3	35·7	7·8	25·5	33·1	35·5
120	..	12·4	41·9	28·5	37·4	9·2	30·7	32·8	35·5
180	..	13·1	43·5	28·5	38·2	10·8	35·0	31·5	37·6

TABLE I C

Graphite sol: Field, parallel to the incident beam but perpendicular to the direction of observation. (Position C)

	Conc. of the sol = 0·0008%					Conc. of the sol = 0·0004%			
	V / H	Darker / Dark	No change / Dark	Dark / Darker		Same as in the previous case			
Field		ρ_v	ρ_h	ρ_u(obs.)	ρ_u(cal.)	ρ_v	ρ_h	ρ_u(obs.)	ρ_u(cal.)
Volt/cm.									
0	..	6·8	26·0	35·5	33·1	7·0	23·6	33·1	34·4
60	..	6·8	34·4	26·2	24·3	7·4	29·0	31·2	30·6
120	..	6·8	47·6	25·5	19·7	7·9	39·4	30·5	25·9
180	..	7·7	54·8	24·7	20·2	8·3	44·8	29·5	24·8

TABLE II A

Stearic acid sol: Average diameter of the particle = 236 m. μ.*
Field: Perpendicular to the incident beam and also to the direction of observation. (Position A)

		Conc. of the sol. = 0·012%				Con. of the sol=0·006%				Sol. =0·003%			
Field volts per cm.	V / H	Brighter / Bright	Bright / Brighter	Brighter / Bright		Same as in the previous case				Same as in the previous case			
		ρ_v	ρ_h	ρ_u(obs.)	ρ_u(cal.)	ρ_v	ρ_h	ρ_u (obs)	ρ_u (cal.)	ρ_v	ρ_h	ρ_u (obs.)	ρ_u (cal.)
0	..	3·9	54·4	12·8	10·7	2·3	58·9	7·7	6·3	1·8	58·4	5·8	4·9
100	..	3·0	31·0	11·6	12·5	1·3	37·0	6·2	4·6	0·9	40·3	4·2	3·2
180	..	2·0	25·1	10·2	10·0	1·1	33·9	5·5	4·2	0·9	37·6	3·9	3·5

TABLE II B

Stearic acid sol: *Field*: *Perpendicular to the incident beam but parallel to the direction of observation.* (*Position B*)

Field volts per cm.	V H	Conc. of the sol. =0·012% Darker Dark	Dark Darker	Darker Dark		Con. of the sol. =0·006% Same as in the previous case				Con. of the sol. =0·003% Same as in the previous case			
		ρ_v	ρ_h	ρ_u(obs.)	ρ_u(cal.)	ρ_v	ρ_h	ρ_u (obs.)	ρ_u (cal.)	ρ_v	ρ_h	ρ_u (obs.)	ρ_u (cal.)
0	..	5·3	49·8	11·5	15·3	4·1	41·5	9·8	13·6	2·9	41·2	8·8	9·7
180	..	7·6	61·0	14·9	18·6	5·5	48·3	11·7	16·0	4·3	45·2	10·4	13·2

* The depolarisation factors for zero field in the case of stearic acid are not uniform in these tables on account of the high secondary scattering of the white sol resulting in the variation of depolarisation at different positions of the cell as shown by Subrahmanya and others [9]

TABLE II C

Stearic acid sol: *Field : Parallel to the incident beam but perpendicular to the direction of observation.* (*Position C*)

Field volts per cm.	V H	Conc. of the sol. =0·012% Darker Dark	Dark Darker	Darker Dark		Con. of the sol. =0·006% Same as in the previous case				Con. of sol. 0·003% Same as in the previous case			
		ρ_v	ρ_h	ρ_u(obs.)	ρ_u(cal.)	ρ_v	ρ_h	ρ_u (obs.)	ρ_u (cal.)	ρ_v	ρ_h	ρ_u (obs.)	ρ_u (cal.)
0	..	2·7	28·5	11·3	11·8	2·4	42·8	7·6	7·8	1·7	45·8	6·4	5·4
180	..	4·2	33·9	14·4	16·0	3·2	42·5	9·7	10·5	2·4	46·2	7·9	7·4

TABLE III A

Vanadium pentoxide sol: Average diameter of the particle 600 m. μ. Field: Perpendicular to the incident beam and also to the direction of observation. (Position A)

Field volts per cm.	V H	Con. of the sol = 0·022%				Con. of the sol. = 0·011%				Con. of the sol. = 0·006%			
		Brighter Bright	Bright Dark	Bright Dark		Same as in the previous case				Same as in the previous case			
		ρ_v	ρ_h	ρ_u(obs.)	ρ_u(cal.)	ρ_v	ρ_h	ρ_u (obs.)	ρ_u (cal.)	ρ_v	ρ_h	ρ_u (obs.)	ρ_u (cal.)
0	..	7·2	100·1	14·1	13·4	6·8	90·7	14·1	13·4	7·2	78·2	15·7	15·3
100	..	3·4	159·2	7·7	5·4	3·2	169·8	6·0	5·0	3·4	161·5	6·2	5·4
180	..	2·9	252·2	5·2	4·0	2·0	290·0	3·7	2·9	2·0	230·0	3·6	4·1

TABLE III B

Vanadium pentoxide sol: Field: Perpendicular to the incident beam but parallel to the direction of observation. (Position B)

Field volts per cm.	V H	Con. of the sol = 0·022%				Con. of the sol. = 0·011%				Con. of the sol. = 0·006%			
		Darker Dark	Darker Dark	Darker Dark		Same as in the previous case				Same as in the previous case			
		ρ_v	ρ_h	ρ_u(obs.)	ρ_u(cal.)	ρ_v	ρ_h	ρ_u (obs.)	ρ_u (cal.)	ρ_v	ρ_h	ρ_u (obs.)	ρ_u (cal.)
0	..	7·2	100·1	14·1	13·4	6·8	90·7	14·1	13·4	7·2	78·2	15·7	15·3
180	..	8·7	87·0	19·5	17·1	8·1	56 8	20·4	20·8	8·6	54·8*	23·4	22·2

* The accuracy is not very high due to faint images.

TABLE III C

Vanadium pentoxide sol: *Field*: *Parallel to the incident beam but perpendicular to the direction of observation.* (*Position C*)

Field volts per cm.	V H	Con. of the sol = 0·022%				Con. of the sol. = 0·011%				Con. of the sol. = 0·006%			
		Darker Dark	Darker Dark	Darker Dark		Same as in the previous case				Same as in the previous case			
		ρ_v	ρ_h	ρ_u(obs.)	ρ_u (cal.)	ρ_v	ρ_h	ρ_u (obs.)	ρ_u (cal.)	ρ_v	ρ_h	ρ_u (obs.)	ρ_u (cal.)
0	..	7·2	100·1	14·1	13·4	6·8	90·7	14·1	13·4	7·2	78·2	15·7	15·3
180	..	7·0	92·0	16·3	13·6	7·8	49·0	21·4	22·0	7·4	56·4*	20·8	19·1

* Due to darkening, not very accurate.

TABLE IV A

Benzo-purpurine sol: *Field*: *Perpendicular to the incident beam and also to the direction of observation.* (*Position A*)

Field volts per cm.	V H	Conc. of the sol = 0·018%				Con. of the sol. = 0·009%			
		Bright No change	No change Bright	Bright Brighter		Same as in the previous case			
		ρ_v	ρ_h	ρ_u (obs.)	ρ_u (cal.)	ρ_v	ρ_h	ρ_u (obs.)	ρ_u (cal.)
0	..	9·0	26·2	40·3	40·0	7·8	26·2	35·0	35·0
60	..	8·4	14·4	57·6	61·5	7·5	14·6	49·8	54·8
120	..	7·5	10·8	64·6	70·9	6·8	11·6	59·7	61·0
180	..	6·7	9·6	72·4	72·4	6·9	9·7	67·5	73·0

TABLE IV B

Benzopurpurine sol: *Field*: *Perpendicular to the incident beam but parallel to the direction of observation.* (*Position B*)

Field volts per cm.	V H	Conc. of the sol. = 0·018%				Conc. of the sol. = 0·009%			
		Dark Darker	Dark Darker	Dark Darker		Same as in the previous case			
		ρ_v	ρ_h	ρ_u(obs.)	ρ_u(cal.)	ρ_v	ρ_h	ρ_u(obs.)	ρ_u(cal.)
0	..	9·0	26·2	40·3	40·0	7·8	26·2	35·0	35·0
180	..	8·7	43·2	27·8	26·7	8·3	47·6	24·0	23·8

TABLE IV C

Benzopurpurine sol: *Field, parallel to the incident beam but perpendicular to the direction of observation.* (*Position C*)

Field volts per cm.	V H	Dark Darker	Dark Darker	No change dark		Same as in the previous case			
		ρ_v	ρ_h	ρ_u(obs.)	ρ_u(cal.)	ρ_v	ρ_h	ρ_u(obs.)	ρ (cal.)
0	..	9·0	26·2	40·3	40·0	7·8	26·2	35·0	35·0
180	..	7·6	36·1	26·4	26·7	6·1	38·8	20·5	20·6

TABLE V

Direction	Graphite	Stearic acid	Vanadium pentoxide	Benzopurpurine
No Field	Order of decreasing brightness V_v, H_h, V_h and H_v. Very little difference between V_h and H_v	Same as in the case of graphite but the beams were not as sharp as with graphite but had a divergent appearance	Order of brightness was the same as with graphite but V_v was extraordinarily bright while the other three components were weak and were of the same order of intensity	Same as with graphite but H_v and V_h although equal were very feeble inintensity
Perpendicular to the incident beam and also to the direction of observation	V_v and H_h brighten up. H_v and V_h practically unaffected	Same as with graphite. V_v increases in brightness much more than H_h. Images are quite sharp	V_v brightens up appreciably. H_v and V_h slight increase in intensity, H_h very slight darkening	V_v slight increase in brightness. H_h large increase in brightness. V_h and H_v not much affected
Paralell to the incident beam but perpendicular to the direction of observation	V_v and H_v slight darkening. V_h not much change H_h darkening. V_h brighter than H_v	Same as with graphite	All components darken. Order of decreasing brightness : V_v, V_h, H_h and H_v *i.e.*, V_h is brighter than H_v	V_v, H_v and V_h slight darkening. H_h appreciable darkening
Perpendicular to the incident beam but parallel to the direction of observation	V_v and H_h darken. V_h slight darkening. H_h no change. H_v slightly brighter than V_h	Same as with graphite but V_h is slightly brighter than H_v	V_v only slight darkening. H_h enhanced darkening. V_h, H_v slight darkening. Order of brightness : V_v, H_h, H_v and V_h	Same as in the case of V_2O_5. But difficult to judge the intensities of H_v and V_h as they were very feeble

Influence of the Electric Field on V_v, H_v, V_h and H_h

The relative variations in the intensities of V_v, H_v, etc., were next studied for all the sols by employing the method of double-image prism described in detail by Krishnan.[1] During this investigation the original beam of light was split up into two beams of equal intensity one vertically polarised and the other horizontally polarised. The light scattered by these two beams on their passage through the colloid, was viewed at right angles by means of a second double image prism, thus seeing all the four components (V_v, H_v, V_h and H_h) simultaneously. On application of the electric field these components changed in their intensities and the results given in Table V were obtained.

DISCUSSION

Effect of intensity of the field on ρ_u, ρ_v, and ρ_h.—Reference to Table I A indicates that with an increase in the field strength there is a variation of ρ_u, ρ_v and ρ_h each of which approaches a limiting value when the field is about 300 volts per cm. This shows that at this field strength all the colloidal

particles get oriented and further increase in the field strength does not alter this orientation. Similar results are also obtained by Krishnan for graphite sols when magnetic fields are employed.

Effect of Dilution of the Sol.—Dilution of the sol brings about a change in the value of ρ_v, ρ_h, and ρ_u as observed by Subramanya and others.[3] But in the the present investigation the solutions could not be diluted indefinitely since the measurements of changes in the values of ρ_v, ρ_h, etc., could not be very accurate on account of diminution of the scattered light with high dilutions. Graphite sol however is comparatively insensitive to changes in dilution.

Effect of Electric Field

Graphite Sols.—Reference to Table I A indicates that the values of ρ_v and ρ_h diminish with the application of the electric field while in the case of ρ_u this value increases. For the other two positions of the electric field however (Tables I B and I C) opposite results are noticed, *i.e.*, the values of ρ_v and ρ_h increase with the application of the electric field while those of ρ_u diminish. A comparison of these results with those of Krishnan reveals the following interesting facts: (1) For positions B and C the values of ρ_h increase both with the electric and the magnetic fields. (2) The value of ρ_v however, increases considerably when the field is applied in position B, while it remains practically constant for positions C. These results are also in qualitative agreement with the results obtained by the use of magnetic field. Thus the orientation of the colloidal particles by the electric and the magnetic fields produce similar effects on ρ_v and ρ_h. In the case of ρ_u on the other hand the electric and the magnetic fields give similar results in positions A and C; but in position B, the electric field diminishes the value of ρ_u while the magnetic field shows a small increase in the value (*i.e.*, from 19·8 to 25·4). This result remains unexplained.

The value of ρ_u has also been calculated by employing the reciprocity relation $\rho_u = \dfrac{1+\frac{1}{\rho_h}}{1+\frac{1}{\rho_v}}$ and these values are given in each of the tables. It is seen that in Table I A the observed and the calculated values agree very much better than those in Tables I B and I C. Krishnan has also made similar observations which have been explained to be due to the specific orientations of the colloidal particles.

Stearic acid sols.—It is well known that stearic acid sols contain anisotropic colloidal particles as evidenced by their twinkling under the ultra

microscope and also by the Schlierung experiments. These particles have been shown by Subramanya and others[3] to consist of disc-shaped particles like those of graphite. Hence stearic acid sols can be expected to be similar to graphite sols in their behaviour towards the depolarisation of the scattered light. Reference to Tables II A, II B and II C shows that with the application of field the values of ρ_v and ρ_h decrease for position A, but increase for positions B and C. Similar change is also noticed with the graphite sols. But the analogy breaks down when the values of ρ_u are taken into consideration. Thus with graphite the values of ρ_u increases when the field is applied for position A and diminish for positions B and C. But in the case of stearic acid the opposite effect is noticed, *i.e.*, a diminution of ρ_u for position A and an increase for B and C. These observations indicate that the variations of ρ_u with the electric field cannot be employed to ascertain the shape of the colloidal particles, since this value is dependent upon both ρ_v and ρ_h. As in the case of graphite, the calculated and observed values of ρ_u are in better agreement for the field position A than for positions B and C.

Vanadium Pentoxide sols.—A study of Tyndall scattering using vanadium pentoxide sols in flow experiments has revealed definitely that the pentoxide particles are rod shaped. This is further confirmed by experiments on double refraction. Results of Table III A indicate that the application of electric field diminishes the value of ρ_v and enhances the value of ρ_h while in the case of graphite (Table I A) the values of both ρ_v and ρ_h get diminished under similar experimental conditions. This is due to the orientation of the rod shaped particles in the vertical position which enhances the vertical component of the scattered light; the enhancement of the vertical component of the scattered light not only diminishes ρ_v but also increases ρ_h. For position B on the other hand the value of ρ_v increases both with graphite and with vanadium pentoxide sols; for position C, ρ_v remains unaltered for both the sols. With respect to ρ_h, the two sols behave differently for these two positions; graphite shows an increase in the value of ρ_h while vanadium pentoxide indicates a diminution in this value. Thus a study of the variation of ρ_v and ρ_h on the application of electric field can enable us to distinguish between the rod shaped particles and disc shaped particles.

Benzopurpurine sols.—The shape of benzopurpurine particles has been investigated by Fraundlich[7] and Subramanya[3] and these authors come to the conclusion that the particles are rod shaped. But a comparison of the Tables I A, I B and I C., with IV A, IV B and IV C. indicate that the behaviour of the benzopurpurine sol with respect of light scattering is more analogous to graphite sol, than to vanadium pentoxide sol. This result

is surprising. It has to be pointed out however, that in the case of benzopurpurine sol, the anisotropy increases with the age, the dye concentration and the salt concentration of the sol. In the present investigation, the sol was only two weeks old and there was practically no salt in the sample. Under these conditions it is probable that the sol particles may not be rod-shaped as observed by other authors. The anisotropy could not be increased by taking a concentrated solution since concentrated solutions are highly conducting.

Studies with double double-image prisms.—The results on the variations of intensities of V_v, H_v, etc., are given in Table V and require a detailed consideration. Sir Raman[8] has pointed out that for particles having random orientation the following relationships hold good.

If the particles are not very small but are spherical and isotropic

$$V_v \neq 0,\ H_v = V_h = 0,\ H_h \neq 0 \qquad (1)$$

or $$\rho_v = \frac{H_v}{V_v} = 0 \text{ and } \rho_h = \frac{V_h}{H_h} = 0.$$

If particles are very small but are not spherical and isotropic

$$V_v \neq 0,\ H_v = V_h = H_h \neq 0 \qquad (2)$$

i.e., $$\rho_v > 0 \text{ and } \rho_h = 1.$$

If the particles are neither small nor spherical and isotropic then

$$V_v \neq 0,\ H_v = V_h = 0,\ H_h \neq 0 \qquad (3)$$

i.e., $$\rho_v > 0 \text{ and also } \rho_h > 0.$$

When these relationships are applied to the sols that have been studied in this paper, it will be noticed that in the case of stearic, benzopurpurine and graphite sols, relationship (3) holds good indicating thereby that the particles are neither small nor spherical and isotropic. This is further confirmed by other evidences already pointed out. Vanadium pentoxide sol obeys relationship (2) showing thereby that the particles are small but not spherical and isotropic. All these predictions are satisfied by the observations recorded in this paper.

The Tyndall scattering in the case of oriented particles appears to be more complicated. Fraundlich[7] has discussed the variation of the total intensity of the Tyndall scattering when the colloidal particles are made to orient by the flow method ; but he has not studied the variations in ρ_v, ρ_h and ρ_u. Subramanya and others[3] have applied the Rayleigh theory of scattering to colloidal particles and have shown that their observations are not in accordance with the theoretical predictions. They have formulated

the "Reflection Rule" which is summarised in Table VI for disc or rod shaped particles.

TABLE VI

Effect of Electric Field on V_v, H_v, V_h and H_h

Direction of Field	V_v	H_v	V_h	H_h
Position A ..	++	+	+	++
,, B ..	−	−	−	−
,, C ..	−	−	−	−

Where ++ indicates strong brightening on the application of field.
+ ,, moderate ,, ,,
− ,, darkening on the application of the field.

The results stated in Table V are in agreement with the predictions of Subramanya[3] except in the case of vanadium pentoxide where a slight darkening is noticed for H_h in position A. The theory of Subramanya[3] when applied to predict the variations of ρ_v and ρ_h for the position A indicates that

$$\rho_v = \frac{H_v}{V_v} = \frac{+}{++} \qquad (1)$$

i.e., diminution on the application of the field.

$$\rho_h = \frac{V_h}{H_h} = \frac{+}{++} \quad \text{do} \qquad (2)$$

According to this theory both ρ_v and ρ_h should decrease on the application of the electric field. This prediction has been true in all the cases studied in this paper except in the case of vanadium pentoxide. Further the reflection rule cannot predict the variations in ρ_v and ρ_h in positions B and C since in both those cases the scattered light gets diminished on the application of electric field. In conclusion it can be stated that the variation of ρ_v and ρ_h on the application of the electric field can enable one to distinguish between the rod shaped and disc shaped colloidal particles. Work on a few more colloidal sols having rod shaped particles is in progress to test out the ideas put in this paper. The authors are deeply grateful to Sir C. V. Raman for his instructive discussions and to Sir J. C. Ghosh for his keen interest and helpful suggestions during the course of the work.

Summary

1. The variation of ρ_u, ρ_v and ρ_h under the influence of electric field has been investigated using the following colloidal systems: (1) Graphite, (2) Stearic acid, (3) Vanadium pentoxide, (4) Benzopurpurine.

2. The variations of ρ_u, ρ_v and ρ_h are studied using the electric field (1) perpendicular to the incident beam and the direction of observation, (2) perpendicular to the incident beam but parallel to the direction of observation and (3) parallel to the incident beam and perpendicular to the direction of observation.

3. The variation in the depolarisation factors depends upon (*a*) the voltage applied, (*b*) the direction of the field, (*c*) the concentration of the solution employed.

4. The effect of the electric field on the variations in intensity of V_v, H_v, V_h and H_h have been carried out using the double double-image prism method.

5. The relationship between the anisotropy of the colloidal particles and the influence of the electric field on the depolarisation factors, is discussed.

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